

The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Nature of the Polysaccharide Hydrolysis in
Black Gumwood Treated with Water at 160°C.

Leo J. Bernardin

June, 1958

THE NATURE OF THE POLYSACCHARIDE HYDROLYSIS
IN BLACK GUMWOOD TREATED WITH
WATER AT 160°C.

A thesis submitted by

Leo J. Bernardin

B.S. in Chem. 1952, Tufts College
M.S. 1954, Lawrence College

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1958

TABLE OF CONTENTS

GLOSSARY	iv
INTRODUCTION	1
APPROACH TO THE PROBLEM	3
LITERATURE REVIEW AND BACKGROUND TO THE PROBLEM	5
EXPERIMENTAL PROCEDURES	10
Hydrolysis Technique and Procedure	10
Apparatus	10
Wood Preparation	12
Hydrolysis Procedure	13
Isolation of the Polysaccharides Remaining in the Tissue After Graded Hydrolysis	15
The Hemicelluloses	15
Intermediate Treatment of the Hydrolyzed Woods	15
Isolation of the Hemicellulose Fractions	18
Purification of the Isolated Hemicelluloses	19
The Alkali-Resistant Celluloses	20
Studies on the Chemical Nature and Polymolecularity of the Hemicelluloses Isolated From the Tissue After Graded Hydrolysis	22
Chemical Analysis	22
Moisture and Ash	22
Uronic Anhydride	23
Hydrolysis and Quantitative Chromatographic Sugar Analysis	23
Determination of the Average Degrees of Polymerization of the Hemicelluloses	24
Studies on the Properties of the Alkali-Resistant Celluloses from the Hydrolyzed Woods	25
Analysis of Component Sugars	25
Molecular Weight Measurements	26
X-ray Diffractions	29
Qualitative Chromatographic Study of the Carbohydrates in the Hydrolysis Liquors	29
EXPERIMENTAL RESULTS	30
Hydrolyzed-Wood Yields	30
Hydrolysis-Liquor Carbohydrates	31

Properties of the Hemicelluloses Remaining in the Tissue	
After Each Stage of Hydrolysis	36
Yields of the Hemicellulose Fractions	36
Chemical Analysis of the Fractions	36
Chain-Length Degradation of the Hemicelluloses	
During Graded Hydrolysis	43
Properties of the Alkali-Resistant Celluloses	
During Graded Hydrolysis	51
Yields and Chain-Length Degradation	51
Analysis of Representative Alkali-Resistant Celluloses	55
X-ray Diffraction Spectra	59
DISCUSSION OF RESULTS	60
SUMMARY AND CONCLUSIONS	67
LITERATURE CITED	72
APPENDIX	76
Quantitative Chromatographic Sugar Analyses	76

GLOSSARY

Zero-minute hydrolysis time-- the point at which the wood has been brought, in contact with the hydrolyzing medium, to the operating temperature of 160°C., and then immediately relieved. This requires 7-9 minutes.

Hydrolysis time-- measured from the point when the system reaches 160°C., i.e. zero-minute hydrolysis time.

Chlorine-ethanolamine residue--the residue remaining after successive chlorinations and alternate extractions of the hydrolyzed wood with alcoholic ethanolamine.

5% Hemicellulose fraction--the material which was extracted from the chlorine-ethanolamine residue with 5% potassium hydroxide, precipitated by acetic acid and ethanol and purified of retained lignin by reprecipitation from solution with ethanol at least twice.

16% Hemicellulose fraction--the material which was extracted with 16% potassium hydroxide from the fibrous residue of the 5% hemicellulose extraction and precipitated from acidified solution with ethanol. The product required little or no purification.

"C" hemicellulose fraction--polysaccharide obtained, after chloriting the residue from the 16% hemicellulose extraction, by extracting with 16% potassium hydroxide and precipitation by acidification with acetic acid and addition of excess ethanol.

Alkali-resistant cellulose--the fibrous residue remaining after extraction of the "C" hemicellulose fraction.

Wood hydrolyzate--the liquor obtained after aqueous hydrolysis of the wood.

Acid-insoluble material--the insoluble material remaining after acidic hydrolysis of the hemicellulose fraction to its constituent carbohydrates.

INTRODUCTION

During the past thirty years, few segments of the pulp and paper industry have experienced a more phenomenal growth than that in the dissolving pulp field. This has been the inevitable result of the ever expanding uses which technology has found for cellulose, and the parallel advances made in the methods for its procurement.

Wood pulp has far surpassed cotton as the chief source of chemical cellulose. By 1955, wood cellulose comprised 86% of the textile-grade chemical cellulose consumption in the United States. This represents an increase in production of 100% since 1950, and of 1100% since 1930 (1). Dissolving-grade pulps now comprise nearly 5% of the country's wood-pulp production (2).

Although most of the dissolving pulp manufactured on this continent is sulfite pulp, much of the recent growth has been in the sulfate field. This has been due to the greater versatility of the sulfate process, which permits the utilization of the pines and short-fibered hardwoods.

Pulps produced by the customary sulfate process without pretreatment are unsuited for dissolving purposes. This is due, in part, to the retention of large amounts of hemicelluloses which give rise to derivatives having decidedly different dissolving characteristics from those of cellulose.

Such adverse properties as haze, anomalous viscosity, fouling of steeping liquors, weakening of filament strength and the plugging of spinnerettes are generally attributed in part, at least, to the hemicellulosic components.

Hence, a hydrolysis treatment of the wood was introduced prior to the sulfate cook (3), one of the functions of which was to reduce the amounts of the noncellulosic polysaccharides in the final pulp. With hardwood pulps this pretreatment reduces the pentosan content to less than 2% (15). If the hydrolysis step is omitted, about 15-30% of the pulp yield will be pentosan (4.5).

Generally, the hydrolysis is conducted under mildly acidic conditions. The pH of the medium can be lowered to catalyze the hydrolysis by addition of mineral acids, or through the generation of wood acids (largely acetic) by water alone at higher temperatures.

The reactions involved during hydrolysis of the wood are not well understood. This is particularly true of those affecting the polysaccharide components. Inasmuch as the principal effect desired by prehydrolyzing wood is the ultimate removal of most of the noncellulosic polysaccharides, this study was undertaken to elucidate the nature of the reactions involved, thus serving to further our understanding of the heterogeneous hydrolysis of the polysaccharides in wood under mildly acidic conditions.

APPROACH TO THE PROBLEM

The polysaccharide constituents comprising the cell wall of wood fibers are broadly divided into: 1) the cellulose and 2) the hemicelluloses. The definitions of these components are amply stated in classical texts on the chemistry of wood (6). The hemicelluloses may be subdivided further, and quite arbitrarily, into two or more fractions through differential alkali extractability from the holocellulose of wood. They differ from the cellulose in their lack of crystallinity, greater chemical heterogeneity, and shorter chain lengths, which markedly influence their chemical properties and reactivity, and by their greater ease of hydrolysis.

The present problem was to study the sequence of changes in the properties of the polysaccharides during the hydrolysis of a hardwood under carefully controlled conditions, with a view towards interpreting the nature of the reactions involved. This entailed fractionation of the polysaccharides according to their accessibility to alkali, the determination of their yields, polymolecularities and chemical composition at several carefully controlled stages of hydrolysis. These findings, it was anticipated, should serve in evaluating the comparative degrees of hydrolysis of the various polysaccharide fractions, in addition to some of the factors influencing their removal from the wood during the course of reaction.

The hydrolysis conditions, water at 160°C. for various intervals of time up to 2 hours, were chosen. The temperature and maximum time period were presumably representative of commercial operations in the United States. Black gum, Nyssa sylvatica Marsh or var. biflora (Walt.) Sarg., a typical hardwood, was selected, since this is a species actually used in prehydrolysis-

sulfate dissolving pulp manufacture. The experimental equipment was designed so as to insure rapid temperature equilibration with a maximum of control, so that reaction could be limited to a specified time period at the desired temperature.

LITERATURE REVIEW AND BACKGROUND TO THE PROBLEM

Much literature on the hydrolysis of wood has been published. The early work deals largely with wood saccharification and has been reviewed by Harris (7). The more recent literature on the subject deals primarily with the prehydrolysis-sulfate manufacture of dissolving pulps. Although this work is mostly of a technical nature, geared to establishing optimum pulping conditions, it has some fundamental bearing on the hydrolysis reactions and will be reviewed as far as it is pertinent.

No sharp distinction can be made between the action of dilute mineral acids on wood and the hydrolysis with water. Hydrolysis with water is generally carried out at higher temperatures which favor the generation of catalytic wood acids. Acetic acid is split off readily, and can be obtained from hardwoods in yields of 4-5% at temperatures above 100°C. (8, 9, 10). Other sources of acidity in the liquors are levulinic, syringic, formic and aldobiuronic acids (11, 12, 13). The pH of the aqueous hydrolyzates from hardwoods has a limiting value of 3-4, measured at room temperature, which is reached within 2 hours at temperatures above 160°C. (14, 15, 16, 17, 18).

In the aqueous hydrolysis of wood the hemicelluloses are readily attacked and are, in part, removed from the wood. The hydrolysis becomes progressively slower as the reaction proceeds (15, 19, 20). Within 2-3 hours at temperatures of 160-170°C. it is possible to reduce the pentosan content by 70-80% for such hardwoods as eucalypt (21), sweetgum (15), beech (14), aspen (19, 22) and white birch (16). The last 20% of the hemicellulose is very difficult to remove by hydrolysis alone (15), although further removal occurs in the subsequent sulfate digestion, in bleaching and in the final alkaline purification of dissolving pulp.

The cellulose of wood is believed to be hydrolyzed to a considerably lesser degree than are the hemicelluloses. Husemann, Schulz and Löhmann (23) reported that the heterogeneous hydrolysis of glycosidic linkages was 1500 times faster in the case of isolated xylan than in purified cellulose. Correns (4) prepared prehydrolyzed-sulfate pulps having about the same viscosity as conventional kraft pulps. However, the latter retained considerably more low-polymeric pentosan than did the former. Haas (24) observed that buffering at pH 3.8 was necessary in order to prevent appreciable cellulose degradation.

The yields of alpha-cellulose from the wood, isolated by laboratory delignification, were not reduced by more than about 6% during the mild aqueous hydrolysis of the wood (14, 15). Almost all of this decrease could be accounted for as pentosan (15). However, losses of alpha-cellulose from the wood on subsequent pulping indicate that degradation had occurred during hydrolysis (14, 15, 18, 21, 25). The more severe the hydrolysis procedure the greater was the alpha-cellulose loss (15).

A few viscosity studies on cellulose preparations obtained from prehydrolyzed woods and pulps have been reported. Pulp viscosities are significantly lowered by aqueous prehydrolysis of the wood at temperatures above 160°C. (14, 15, 16). Also, the viscosities of alpha-cellulose and holocellulose preparations, isolated from white birch and beech after aqueous hydrolysis treatments, are significantly decreased when the reaction temperature is above 160°C. (14, 20). The available data, however, are fragmentary and the conclusions derived are open to question.

The fundamental factors governing the hydrolytic removal of the polysaccharides from wood during treatment with water at high temperatures or

with dilute mineral acids are not understood. The heterogeneous composition of the hemicelluloses suggests that certain functional groups which favor solubility may be preferentially dissolved. The polysaccharides extracted by hot water from aspen and birch holocellulose are richer in uronic acids than are the parent polysaccharides (26, 27). Haas (24) found that the polyuronide-to-pentosan ratio of beechwood decreases on treatment with dilute acid at 130°C. However, Foster and others (28) reported the opposite to be true on heating pre-extracted eucalypt wood with normal sulfuric acid at 91°C. for 3 hours. The hydrolytic action of hot water on the composition of the polysaccharides of wood has never been studied.

The hemicelluloses are believed to be heterogeneous in their poly-molecularity (29, 30). Hence, possible preferential dissolution of the lower molecular-weight chains may help to account for the high initial rate of removal of the wood polyoses. Many authors in the field have theorized that aqueous hydrolysis involves the solution of the polysaccharides from the wood followed by further hydrolysis to monosaccharides in the liquor (31, 32, 33). Scharkow (32) even estimates the preliminary extraction to be 5 to 10 times faster than the secondary hydrolysis.

Some work has been published on the polymeric nature of the carbohydrates in the hydrolysis liquor. Schmitz (34) in his early work on the hydrolysis of Douglas-fir recognized that at 120°C. the carbohydrate dissolved from wood was at least partially polymeric in nature. Sohn and Lenel (35) estimated that the aqueous hydrolysis of pine, carried out at 150°C. for 1-2 hours, yields carbohydrates 30-70% of which are still in the

polymeric form. Overbeck and Müller (31), who fractionated the oligosaccharides from the aqueous hydrolysis liquors of beechwood through aqueous-alcoholic precipitations, found chain lengths corresponding to degrees of polymerization as high as 13. Finally, 20 simple sugars and oligosaccharides were separated and isolated by column chromatography in the blowpit liquors of the Masonite process (36), which is essentially an extreme case of rapid aqueous hydrolysis.

The heterogeneous hydrolysis of the polysaccharides in the wood has not been studied. A few attempts have been made to study the kinetics of wood hydrolysis by means of the rate of removal of carbohydrate material from the wood (12, 33, 37). The rate of solution of the carbohydrates from wood is a complex function of many factors, and cannot be used as a measure of polysaccharide hydrolysis. Hence, this work has little bearing on the present subject.

In addition to hydrolysis, the carbohydrate constituents are involved in other chemical changes under the conditions used in commercial hydrolysis treatments of the wood. Carbohydrates undergo thermal decompositions at high temperatures in acidic media yielding products such as furfural, hydroxymethyl furfural and levulinic and formic acids (12, 38). Aronovsky and Gortner (19) found that 50% of the original wood pentosan was destroyed during hydrolysis of aspen at 170°C. for 2 hours. The decompositions follow a first order reaction at high temperatures in dilute sulfuric acid (12).

Pseudolignins are also formed during wood hydrolysis through recondensation and polymerization of these reactive components (14, 19, 35, 39, 40).

In summary, the literature on the hydrolysis of wood emphasizes the

great complexity of factors involved. The hemicellulosic polysaccharides are readily attacked and removed from the tissue, and the cellulose may also be degraded. Fundamental information on the nature of the polysaccharide hydrolysis is lacking. The changes in chemical composition and polymolecularity and their influence on the course of reaction have not been investigated. The present work attempts to fill this gap in our current understanding of the process.

EXPERIMENTAL PROCEDURES

HYDROLYSIS TECHNIQUE AND PROCEDURE

APPARATUS

The apparatus used in the hydrolysis of the wood was designed to allow a maximum of control over the experimental conditions. It was desired to maintain the reaction temperature within 1-2°C., as well as to raise the system quickly to the desired temperature, and to cool it rapidly enough to check the hydrolysis at any predetermined time. These specifications limited hydrolysis to the time interval desired. Rapid equilibration of the system to temperature minimized the uncertainties resulting from a prolonged 'rise-to-temperature' phase of the hydrolysis, which have been commonly associated with all previous studies of this type.

A schematic diagram of the digestion apparatus is shown in Figure 1. It consists of two, series-connected, stainless steel digesters of 40 l. capacity each, and auxiliary equipment for rapid temperature equilibration and control. Digester no. 1 was used as a liquor preheater and no. 2 served as the hydrolysis chamber. The former also served as a rapid cooler for the liquor after hydrolysis. Liquor transfer between the two chambers was effected by the external application of up to 140 p.s.i. of nitrogen pressure to the appropriate vessel.

Each digester was equipped with a concentric pipe heat exchanger supplied with saturated steam up to 150 p.s.i. No. 2 had an additional electric heater embedded in the shell for preheating the walls of the chamber.

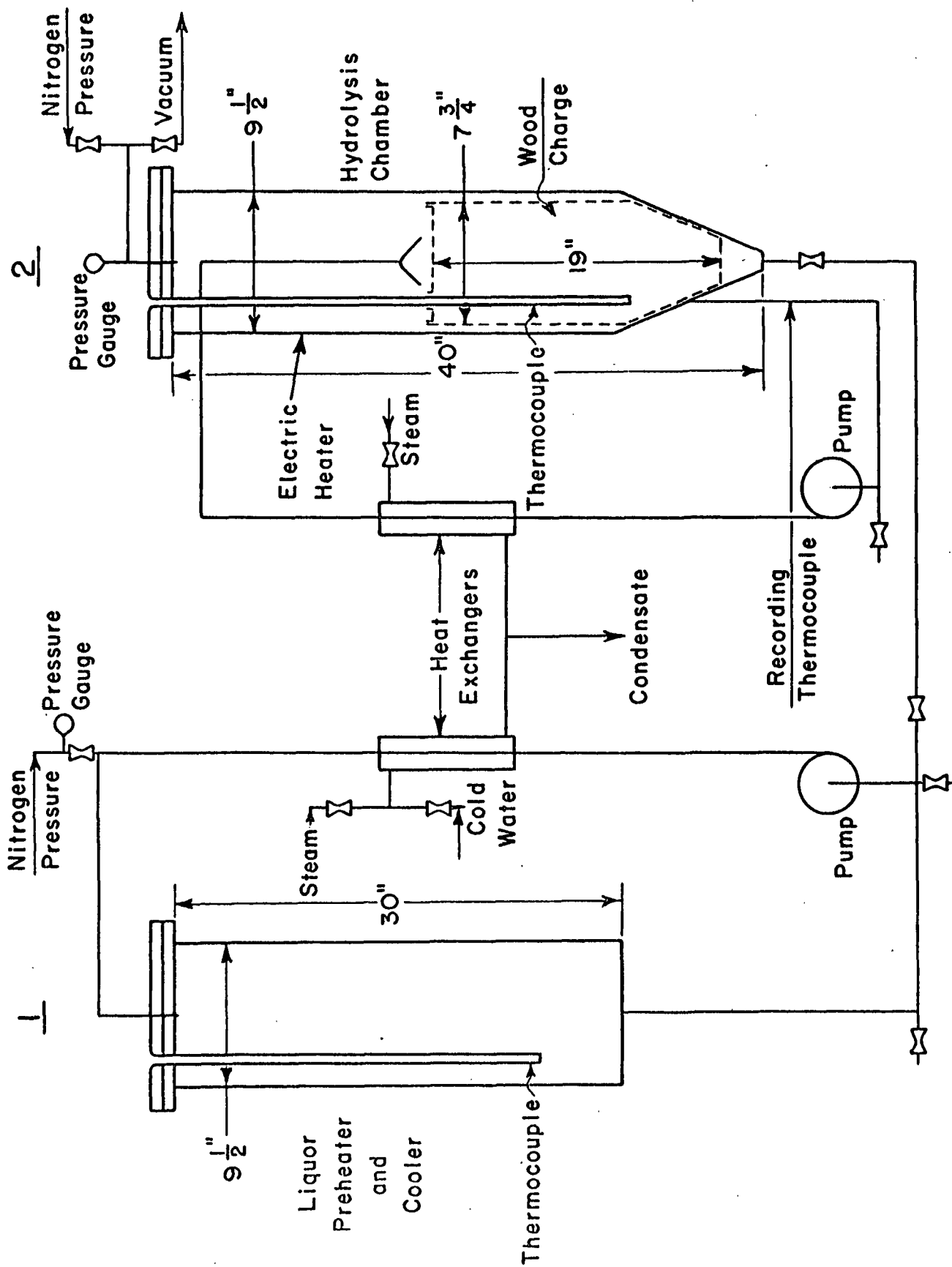


Figure 1. Schematic Diagram of Hydrolysis Apparatus

Centrifugal pumps were located in the circulation lines to maintain temperature uniformity and a high rate of heat transfer. All surfaces contacting the liquor were of stainless steel.

Temperatures in the preheater and hydrolysis chamber were measured with chromel-alumel thermocouples, calibrated with a Bureau of Standards thermometer. A Leeds and Northrup, student potentiometer was used in the thermocouple circuits to obtain the temperature measurements. In the hydrolysis chamber, the thermocouple was immersed within the wood charge and a second, recording-type, iron-constantan couple was located in the circulation line thus permitting a measure of temperature throughout the system.

The digester capacities (40 l. each) were large enough so that single-batch hydrolyses of enough wood could be made to meet the later analytical requirements of the proposed experimental program. The wood charge (about 1 kg. of wood shavings) in the hydrolysis chamber was held in a basket made of 40 by 60 mesh stainless-steel screening.

WOOD PREPARATION

Ten, 5-foot bolts of black gum were obtained from the Texas forest holdings of the Champion Paper and Fibre Co. The sample was identified as Nyssa sylvatica Marsh or its variety biflora (Walt.) Sarg. from the twigs and the leaves by Dr. Isenberg (41). The barked logs measured 6 1/2 to 8 1/2 in. in diameter, with about 1 1/4 to 1 1/2 in. of heartwood. An 8-in. log showed about 20 growth rings to the inch and the trees were approximately 70 years old. The wood was green and had a moisture content of 45% (on the green basis).

The barked logs were reduced to shavings with a commercial planer, and the shavings were screened on a shaker screen to remove sawdust and large pieces. The fraction retained by a 4-mesh screen was used. These shavings averaged about 1 mm. in thickness, varying between about 0.3 and 2.6 mm. All shavings were air dried to a moisture content of about 5% prior to screening.

Shavings were preferred to chips in the hydrolysis study, since the latter would have provided a significant temperature gradient from the outside surface to the center. The use of shavings served as a means of effecting temperature uniformity within the system.

HYDROLYSIS PROCEDURE

A series of five aqueous hydrolyses were carried out at 160°C. by using increasing time intervals, namely 0, 15, 30, 60 and 120 minutes. The hydrolyzing medium was distilled water. Between 18 and 19 kg. of distilled water, weighed to the nearest 10 g. were placed in the preheater (digester no. 1 in Figure 1) and brought to a temperature of 170°C. The shell of the hydrolysis chamber (digester no. 2) was preheated electrically to a surface temperature of about 160°C. At this point, no. 2 digester was charged with about 1 kg. of wood shavings of predetermined moisture content, carefully weighed and enclosed in the wire-mesh basket. The digester was then sealed and evacuated.

Hydrolysis was started by blowing the preheated water under a maintained nitrogen pressure of 140 p.s.i. from the preheater into the hydrolysis

chamber. During this injection the water temperature dropped to between 120 and 140°C. However, the system was brought to the operating temperature of 160°C. by means of the heat exchanger and electric booster in 7 to 9 minutes. The liquor-to-wood ratio was about 18 to 1. The point represented by "zero minutes" in the series was arbitrarily chosen as that point at which the system had reached a temperature of 159 to 160°C. Hydrolysis time for the other intervals was measured from this point.

Digestion was stopped when the desired time had elapsed, by discharging the liquor from the hydrolysis chamber back into no. 1 digester under nitrogen pressure. Further hydrolysis of the liquor components was prevented by rapid cooling of the hydrolyzate through the cold water heat exchanger in the no. 1 digester. The wood temperature was also rapidly lowered by releasing the hydrolysis chamber to the atmosphere, after completion of the liquor transfer. The amount of steam and volatiles flashed during this step was estimated by recondensing them in an ice-water bath. No water washes of the woody residues were used.

Material balances and wood yields were determined for each stage of hydrolysis from the amounts of reactants and products. These required a knowledge of the weights of the initial wood and water, resulting liquor, residual wood, liquor retained by this wood, residual condensibles in the preheater and hydrolysis chamber, the moisture contents of the air-dried, original, and hydrolyzed wood shavings, and the nonvolatile solids content of the liquor. The development of acidity in the hydrolysis liquors was determined by pH measurements at 25°C.

ISOLATION OF THE POLYSACCHARIDES REMAINING IN
THE TISSUE AFTER GRADED HYDROLYSIS

THE HEMICELLULOSES

Intermediate Treatment of the Hydrolyzed Woods

The present investigation was directed primarily towards a study of the action of the hydrolysis on the polymeric and chemical nature of the wood polysaccharides. Thus, it was essential that these carbohydrates be isolated quantitatively and that their properties should represent as nearly as possible those found in the residual wood, after each of the hydrolytic treatments. Since the hemicelluloses cannot be extracted quantitatively directly from the wood, preliminary delignification of the wood was essential. This involved the preparation of a holocellulose prior to their extraction with alkali. Since all of the common methods for holocellulose preparation incorporate the use of chlorine in one of its oxidative states, the highly labile hemicelluloses may be changed further during isolation.

Wethern (29) made an extensive study of the influences of the various holocellulose procedures on the yields and viscosities of the isolated hemicelluloses of spruce. His results indicate that a modified Thomas procedure (26) yielded hemicelluloses most suitable for physicochemical studies. Thompson and Wise (30) found that the Wethern procedure affected the average degrees of polymerization of the hemicelluloses very little (in the case of aspen). Finally, the nonaqueous media used in this method would preclude the loss of significant amounts of low molecular weight polysaccharide from the hydrolyzed woods.

Hence, the Wethern procedure, with slight modifications (30) was used in the isolation of the hemicelluloses. The method combines a series of chlorinations of the wood suspended in carbon tetrachloride at 0 to 5°C., alternated by extractions of the chlorolignins with alcoholic ethanolamine. The residue from this procedure, in the case of black gum, was still highly lignified, but sufficient chlorination of the lignin resulted to permit its coextraction by means of alkali together with the hemicelluloses. The lignin remained largely in solution when the polysaccharides were precipitated from acidified solutions by alcohol. Contamination of the hemicelluloses by adsorbed lignin was minimized by repeated solution in alkali and precipitation.

The following procedure was used: wood shavings remaining after each stage of the hydrolysis, and also from the original wood, were reduced separately to a coarse meal in a Wiley mill and fractionated, with retention of the 30 to 80-mesh fraction. A carefully weighed sample of about 100 g. of the selected fraction was pre-extracted with 95% ethanol at room temperature for at least 16 hours, with occasional stirring, to remove some of the lignin and extraneous components. Moisture was then introduced to activate the system by thoroughly wetting the wood with 50% aqueous ethanol at 0°C. just prior to chlorination.

The chlorinating reagent was prepared by absorbing chlorine gas in carbon tetrachloride at -10 to -5°C. for at least 30 minutes. The chlorinator consisted of a coarse, fritted-glass funnel, 12.5 cm. in diameter, surrounded by a cooling bath and connected with a 4-l. suction flask. A

50% aqueous ethylene glycol solution, maintained at -5°C . by an external refrigerator, was circulated through the cooling bath so as to maintain the temperature. A motor-driven glass stirrer insured uniform mixing of reactants and uniform cooling.

The wood meal, pretreated as described above, was slurried with 500 ml. of c.p. carbon tetrachloride at about -5°C . in the chlorinator. A back pressure of about 6 in. of water was applied to the suction flask to prevent loss of liquid through the funnel. The chlorinating reagent at -10 to -5°C . was then added according to the schedule described below, and the reaction was continued for 10 minutes. During the reaction, which is highly exothermic, the temperature was maintained between 0 and 5°C . by vigorous stirring in the cooling bath and by further dilution with c.p. carbon tetrachloride at -5°C . The reaction was stopped after 10 minutes by drawing off the partially spent chlorine solution by suction, and then neutralizing the residue by two thorough washings with a 3% alcoholic solution of ethanolamine. This was followed by two 5-minute washings with the same reagent at room temperature, and finally by two washings with 95% ethanol.

The entire procedure was repeated twice, beginning with the 50% aqueous ethanol pretreatment. The procedure for each chlorination step may be summarized as follows:

1. Activation of the wood with 50% aqueous ethanol at 0°C .
2. Dispersion of the meal in 500 ml. of c.p. carbon tetrachloride at -5°C .
3. Chlorination by the addition of 500 ml. of chlorinating reagent at about -5°C .

4. Time of reaction, 10 minutes.
5. Temperature of reaction, 0-5°C.
6. Temperature controlled by the occasional addition of up to 250 ml. of c.p. carbon tetrachloride at -5°C.

For the wood samples remaining after 30, 60 and 120 minutes of hydrolysis, the first stage of the chlorination was so vigorous that the chlorine addition had to be cut in half so as to maintain temperature control. The second and third chlorinations, however, were conducted in accordance with the standardized schedule described.

Before air-drying the final chlorine-ethanolamine residues, two washes were given with c.p. acetone.

Isolation of the Hemicellulose Fractions

The hemicelluloses were extracted from the respective chlorine-ethanolamine residues by the procedure used by Wise, Murphy and D'Addieco (42) for chlorite holocelluloses. This consists of successive 5- and 16%-potassium hydroxide extractions, to yield the respective "5" and "16%" hemicellulose fractions, after acidification with acetic acid and alcoholic precipitation of the extracts. The 5% hemicelluloses represent the more accessible fraction, and the 16% complement, the less accessible fraction.

The extractions were carried out in 2-liter Erlenmeyer flasks, each fitted with a dropping funnel and two right-angle bends with stopcocks attached. Duplicate 20-g. samples of chlorine-ethanolamine residue were placed in separate flasks and the air displaced by flushing with nitrogen

for 15 to 30 minutes. A volume of 400 ml. of 5% potassium hydroxide solution was then added through the dropping funnel. The flasks were sealed off from the atmosphere with stopcocks, and swirled occasionally for two hours at 20°C. Subsequently, the contents of the flasks were filtered through 60-mm., coarse, fritted-glass funnels into 100 ml. of glacial acetic acid. The residues were thoroughly washed with 300 ml. of 5% potassium hydroxide followed by 60 ml. of distilled water.

The combined filtrates and washings, which were acid, were immediately precipitated into a large enough excess of ethanol to give a final alcoholic concentration of 80-88%. The alcoholic strength was increased to the higher value in precipitating polysaccharides from the more severely hydrolyzed woods.

The residue from the 5% extraction was then neutralized with dilute acetic acid, and the extraction procedure repeated using 16% potassium hydroxide. The volume of glacial acetic acid to acidify this extract, prior to alcoholic precipitation was 300 ml. The fibrous residue from this extraction was neutralized with dilute acetic acid and set aside for the cellulose isolation.

Purification of the Isolated Hemicelluloses

As was previously mentioned, the hemicelluloses required purification due to coprecipitated lignin. The procedure entailed resolution of the crude polysaccharides in 100 ml. of the same strength potassium hydroxide as that used in the original extraction, acidification with acetic acid,

and reprecipitation by pouring into 2500 ml. of absolute ethanol. The minimum ratio of alcohol to water used in this step was 10:1. The supernatant alcohol was siphoned off, and the hemicelluloses were isolated from the remaining suspension by centrifuge. The polysaccharide was washed twice with boiling, absolute ethanol, 2-4 times with anhydrous ether and air dried.

The 5% hemicelluloses from the several hydrolysis stages and from the original wood were reprecipitated at least twice, resulting in a marked color improvement. However, all the purified hemicelluloses from the hydrolyzed woods were tan colored when air dried, and gave straw-colored solutions. The longer the hydrolysis, the darker were the isolated hemicelluloses. Inasmuch as most of the chlorolignins had been removed from the chlorine-ethanolamine residue by the 5% extraction, the 16% hemicelluloses required little or no reprecipitation. The purification scheme and some of the properties of the hemicelluloses are listed in Table I.

THE ALKALI-RESISTANT CELLULOSES

Ordinarily, the term alkali-resistant cellulose refers to the residue remaining after extraction of the hemicelluloses from a holocellulose with alkali. In this work, however, the residues from the hemicellulose extractions were still partially lignified. Hence, a single chlorite treatment according to the procedure of Wise and others (42) was introduced following the hemicellulose extractions so as to complete the delignification. This was followed by a final extraction with 16% potassium hydroxide to remove a residual amount of hemicellulosic polysaccharides, which was subsequently labeled "hemicellulose C" after alcoholic precipitation from the acidified

TABLE I

PROPERTIES OF THE PURIFIED HEMICELLULOSES

1. Extracted with 5% Potassium Hydroxide

Hydrolysis Time	No. of Re-precipitations	Color	Vanillin & Syringaldehyde ¹	Moule Test
Original wood	2	gray-white	none	faint
0 min.	2	light tan	--	faint
15 min.	2	light tan	--	very faint
30 min.	2	light tan	none	very faint
60 min.	3	light tan	none	masked
120 min.	2	brown	--	masked

2. Extracted with 16% Potassium Hydroxide

Original wood	0	gray-white	--	light
0 min.	0	light tan	--	faint
15 min.	0	light tan	--	very faint
30 min.	1	light tan	--	very faint
60 min.	1	light tan	--	masked
120 min.	1	brown	--	masked

¹ By alkaline nitrobenzene oxidation.

extract. The resulting fibrous residue was then termed arbitrarily "alkali-resistant cellulose".

The detailed procedure for this phase of the cellulose isolation was as follows: The residue from the hemicellulose extractions was transferred back to the 2-l. Erlenmeyer flask and chlorited for 1 hour at 70°C., using 2.0 ml. of glacial acetic acid, 6.0 g. of sodium chlorite and 640 ml. of distilled water. The fibrous product from this treatment was then cooled in an ice bath and washed free of residual chemical with 1 l. of ice-water on a coarse, fritted-glass funnel. After two washings with c.p. acetone and two with anhydrous ether, the chlorited residue was air dried. This was followed up by a final extraction with 16% potassium hydroxide according to the procedure previously described, to yield the "hemicellulose-C" fraction. After neutralizing the fibrous residue with dilute acid, and solvent drying with acetone and ether, the cellulose isolation was complete.

STUDIES ON THE CHEMICAL NATURE AND POLYMOLECULARITY
OF THE HEMICELLULOSES ISOLATED FROM THE TISSUE AFTER
GRADED HYDROLYSIS

CHEMICAL ANALYSIS

Moisture and Ash

The moisture and ash contents of the hemicelluloses were determined, and the polysaccharide yields calculated on the oven-dry, ash-free basis. The moisture content was obtained from the loss in weight on oven drying at 105°C. to constant weight. Sulfated ash was determined according to the procedure of Wise and others (42), and after allowance for siliceous

and other insoluble material, was converted to equivalent potassium. All determinations were made in duplicate.

Uronic Anhydride

The uronic anhydride content of the hemicellulose fractions was measured according to Browning's procedure (43). The procedure was standardized by analyzing pure glucurone.

Hydrolysis and Quantitative Chromatographic Sugar Analysis

The hemicelluloses were hydrolyzed by a two-step procedure (44) in preparation for chromatographic analysis of the constituent sugars. The first step consisted of dissolution and hydrolysis of a carefully weighed, 100-200 mg. sample of the polysaccharide in 2 ml. of 72% sulfuric acid at about 10°C. for 30 minutes. The resulting solution was then diluted, in the second step, to 2% acid with 116 ml. of distilled water and heated to boiling under reflux for 3 hours, so as to complete the hydrolysis.

A weighed amount of ribose, which is not present as a unit in the polysaccharides under investigation, was then added to the hydrolyzate for reference purposes. The amount added, about 60% of the weight of hemicellulose used, was roughly comparable to the xylose content in solution. Since the proportion of ribose to hemicellulose was thus fixed, evaluation of the ratio of each sugar in the hydrolyzate to ribose afforded a measure of the percentage of the corresponding sugar unit in the polysaccharide. This technique permitted the use of aliquots, compensated for possible losses from retention and adsorption of sugar in the neutralization steps to follow, and expedited the analysis.

After addition of the ribose, any insoluble material present in the hydrolyzate was centrifuged off, isolated and weighed. The clear solution was then neutralized with saturated barium hydroxide to a pH of 6. The precipitated barium sulfate was removed by centrifuging, and following extraction of the last traces of barium through cationic exchange with IR-120 resin, the dilute polysaccharide hydrolyzate was concentrated under reduced pressure, at a temperature of about 20°C., to a volume of about 5 ml. This was protected from biological attack by the addition of 20 p.p.m. of pyridose.

The concentrated hydrolyzates were separated into their constituent sugars by paper partition chromatography. A modified method of analysis was developed in co-operation with C. V. Piper (45), and was used exclusively in this work. The chromatographic procedure and method of analysis are described fully in the Appendix.

DETERMINATION OF THE AVERAGE DEGREES OF POLYMERIZATION OF THE HEMICELLULOSES

The average D.P.'s of the hemicellulose fractions were determined from viscosity measurements. The method of Thompson and Wise (30), which has been used by a number of investigators for the study of molecular weights of hemicelluloses (46, 47, 48), was used in this investigation. It entails measurement of the reduced viscosities (η_{sp}/c) of several dilute solutions of the polysaccharide in 10% potassium hydroxide. Extrapolation of the resulting data to zero concentration affords the intrinsic viscosity, $[\eta]$, according to the Huggins equation,

$$\eta_{sp}/c = [\eta] + K [\eta]^2 c, \quad (1)$$

where c is the polymer concentration and K is a system parameter. The

viscosity-average degree of polymerization of the hemicellulose fraction, having a narrow molecular-weight range, is related to the intrinsic viscosity in accordance with Equation (2),

$$[\eta] = K^{\eta} (\text{D.P.}) \quad (2)$$

where K^{η} , evaluated for the hemicelluloses of bigtooth aspen (Populus grandidentata) at 30°C., is 4.4×10^{-3} (29). The value of the constant is in good agreement with those given by Husemann (49) for the hemicelluloses of spruce, beech and wheat straw, and by Wethern (29) for black spruce. The value for D.P., obtained from Equation (2) using the stated value for K^{η} , approaches a number average.

Ostwald-Fenske, no. 50, capillary viscometers were used for measuring the dilute solution viscosities. Duplicate solutions of each of the 5 and 16% hemicellulose fractions, obtained from the original wood and from the several hydrolyzed woods, were made up in 10% potassium hydroxide. The duplicate solutions were then diluted further with one and two volumes each of 10% potassium hydroxide, and the specific viscosities measured. The data were then plotted as a function of solution concentration, and the linear plots obtained were extrapolated to zero concentration for evaluation of the intrinsic viscosity of each polysaccharide.

STUDIES ON THE PROPERTIES OF THE ALKALI-RESISTANT CELLULOSES FROM THE HYDROLYZED WOODS

ANALYSIS OF COMPONENT SUGARS

Three alkali-resistant cellulose samples from different stages of the wood hydrolysis were analyzed chromatographically to determine the nature

and amounts of the nonglucosidic sugar components. The celluloses were taken from the 0-, 30- and 120-minute hydrolyses to give a cross-sectional representation of the hydrolytic action on the composition of the wood cellulose*.

The cellulose samples were hydrolyzed to their constituent sugars according to the Forest Products Laboratory procedure (50). This involved hydrolysis of a 300-mg. sample in 3 ml. of 72% sulfuric acid at 30°C. for 1 hour, followed by dilution with 84 ml. of distilled water and autoclaving for a second hour at a steam pressure of 15 p.s.i. The hydrolyzate was then neutralized with barium hydroxide to a pH of 5, and the precipitated barium sulfate was separated by successive centrifugings and washings. The combined centrifugates were concentrated to a small volume under reduced pressure, and chromatographed on Whatman no. 1 paper for 36 hours in ethyl acetate-acetic acid-formic acid-water, 18:3:1:4. The sugars were analyzed by the method of Piper and Bernardin (45), which is described in the Appendix.

MOLECULAR WEIGHT MEASUREMENTS

The average degrees of polymerization of the alkali-resistant celluloses from the original and hydrolyzed woods were measured viscometrically in cupriethylenediamine solution. Since the viscosity of solutions of cellulose in standardized cupriethylenediamine solvent is a function of polymer concentration and rate of shear in the viscometer, as well as molecular weight, the experimental procedure must be carefully designed to

*The analyses were carried out by Mr. C. V. Piper of the Institute analytical chemistry group.

obtain truly representative chain lengths by this method (51). TAPPI and A.C.S. viscosities do not meet these requirements. By measuring dilute solution viscosities at zero shear rate and extrapolation to zero concentration, the intrinsic viscosity may be obtained which is a direct function of degree of polymerization.

The procedure involved in the determination of viscosity at zero shear rate requires measurement of solution viscosity under at least two different operating pressures and extrapolation of the observed values to zero pressure. Browning and Sell (52) have developed a technique which simplifies the experimental manipulations. A modified Ostwald-Fenske viscometer having two calibrated flow bulbs and a common capillary is used. The flow times of the polymer solution, at concentration c , are measured in both bulbs. The solution viscosity at zero shear rate (η_{∞}) is then calculated from the following equations:

$$\eta_{\infty} = A \rho t_1^2 t_2^2 / (m^2 t_2^2 - t_1^2) \quad (3)$$

$$t^2 = t - B/t \quad (4)$$

The constants A , B , and m^2 are viscometer constants obtained through calibration with appropriate Newtonian fluids, t is observed flow time, the subscripts 2 and 1 refer to the upper and lower bulbs, respectively, and ρ is the solution density. In the particular apparatus used here, $A = 2.994 \times 10^{-2}$, $B_2 = 38.94$, $B_1 = 90.32$, and $m^2 = 4.125$.

From the solution viscosity at zero rate of shear (η_{∞}) and the solvent viscosity (η_0), the specific and reduced viscosities, η_{sp} and η_{sp}/c , respectively are readily calculated:

$$\eta_{sp} = (\eta_{\infty} - \eta_0) / \eta_0 \quad (5)$$

The intrinsic viscosity of the system at zero shear rate, $[\eta]$ is then obtained by extrapolating the logarithm of the reduced viscosity of a number of solutions to zero concentration according to the Martin equation:

$$\log (\eta_{sp}/c) = \log [\eta] + K'[\eta]c \quad (6)$$

where K' is a parameter. Furthermore, although K' is influenced by shear rate, it has been found to be essentially constant at zero rate of shear for celluloses of all but the highest degrees of polymerization. Where c is given in g./100 ml. and the temperature is 25°C., K' is 0.133 (51, 52). Thus, the intrinsic viscosity can be calculated from the reduced viscosity of a single cellulose solution, by using Equation (6).

The degree of polymerization (D.P.) is related linearly to the intrinsic viscosity in cupriethylenediamine in accordance with Equation (7).

$$D.P. = K[\eta] \quad (7)$$

where K was taken as 170 (53).

This method was found to be highly reproducible in the present research. Cupriethylenediamine solvent was supplied by Ecusta Paper Corp., and was carefully analyzed according to TAPPI method T 230 sm-50. The titration was made potentiometrically as suggested by Browning and associates (54). The master solvent analyzed as 1.005M in copper, with a ratio of ethylenediamine to copper of 2.13:1. The cellulose solutions for viscosity measurements contained 50% of the master solvent and 50% water. The sample was first thoroughly wetted with water, and then totally dissolved by the addition of an equal volume of cupriethylenediamine. The solutions were all prepared under an atmosphere of purified nitrogen. The apparatus used for this operation is discussed in the literature (54).

X-RAY DIFFRACTION

It was desired to note if the wood hydrolysis had produced any marked changes in cellulose crystallinity. For this reason, x-ray diffraction spectra were obtained for the alkali-resistant celluloses from the 0- and 120- minute hydrolysis stages. The spectrograms were obtained on a North American Phillips Co. recording x-ray spectrometer.*

QUALITATIVE CHROMATOGRAPHIC STUDY OF THE CARBOHYDRATES IN THE HYDROLYSIS LIQUORS

Liquor samples of from 5 to 10 liters from each of the five hydrolysis stages were concentrated to a few hundred milliliters under reduced pressure at about 15°C. and precipitated into 6 volumes of ethanol. These were stored for a number of months at room temperature for future study.

The supernatant alcoholic solutions, which contained the low molecular-weight carbohydrates, were then concentrated further under reduced pressure and chromatographed. The chromatograms were developed in butanol-pyridine-water 10:3:3 for about 85 hours and sprayed with 3% o-aminobiphenyl solution in glacial acetic acid, containing about 1.5% phosphoric acid (55). The sheets were oven dried and the carbohydrates identified by comparison with appropriate reference sugars.

In addition, the alcohol-insoluble polysaccharides precipitated from the 0- and 30-minute hydrolysis liquors were further hydrolyzed to their constituent sugars and chromatographed.

*Obtained by Dr. Garey of the Institute physical chemistry group

EXPERIMENTAL RESULTS

HYDROLYZED-WOOD YIELDS

The yields of woody fibrous material and other pertinent data from each stage of hydrolysis, and the yields of the residues from the chlorine-ethanolamine procedure are given in Table II.

TABLE II

YIELDS OF WOODY FIBROUS MATERIAL AND OTHER PERTINENT HYDROLYSIS DATA

Hydrolysis Data	Original Wood	Hydrolysis Time in Minutes				
		0	15	30	60	120
Yield of woody fibrous material, ¹ %	100%	95.5	91.5	85.2	77.0	71.6
Wood loss ¹ , %	--	4.5	8.5	14.8	23.0	28.4
Nonvolatile solids in liquor ¹ , %	--	3.6	6.8	11.8	19.9	22.7
Volatile material in liquor, ^{1,2} %	--	0.9	1.7	3.0	3.1	5.7
Liquor pH ³	--	4.80	4.24	4.02	3.54	3.61
Liquor-to-wood ratio	--	17.4	17.2	19.4	18.7	19.8
Yield of chlorine-ethanolamine residue ⁴ , %	105.0 ^{1,5}	102.05	95.3	94.0	93.0	92.5

¹ Percent based on original, oven-dry wood.

² Difference between wood loss and nonvolatile solids in liquor.

³ Measured at 25°C.

⁴ Percent based on oven-dry, hydrolyzed wood.

⁵ High values due to chlorination of lignin which isn't removed.

These data are plotted against time of hydrolysis in Figure 2. In Figure 3, the yield of woody fibrous material is shown to be a linear function of the logarithm of time over the two-hour period. Green and Leaf (56) found a similar relationship in the treatment of pine with boiling water for 60 hours. Of the material removed from the wood used in the present study over the course of reaction, 80% was accounted for as nonvolatile solids in the liquor. The remaining 20%, which is less than 6% of the total wood, is presumed to be volatile hydrolysis and decomposition products, such as furfural and hydroxymethyl furfural, acetic and formic acids, and methanol, but no analytical data were obtained.

The liquor pH reaches a plateau at about 3.5 within the first hour.

HYDROLYSIS-LIQUOR CARBOHYDRATES

The results of the chromatographic studies of the hydrolysis liquor carbohydrates soluble in alcohol are presented in Table III. Identification of the several carbohydrates was made by chromatographic comparison with reference sugars. Visual appraisal of the relative intensities of the chromatographic spots was used as an approximate index of their comparative concentrations in the liquors. In Table III the following semiquantitative classifications in order of decreasing strength were made, using the terms strong, moderate, weak and trace, in describing the progressive appearance of the various sugars in the liquors during the course of hydrolysis.

The sugars resulting from the acidic hydrolysis of the polysaccharides precipitated by alcohol from the 0 and 30-minute liquors were also identified

TABLE III

APPROXIMATE RELATIVE STRENGTHS OF THE ALCOHOL-SOLUBLE
CARBOHYDRATES IN THE AQUEOUS HYDROLYSIS LIQUORS BY
VISUAL APPRAISAL OF THE CHROMATOGRAMS

Carbohydrate	Cold Water Extract of Orig. Wood	Liquor of Wood Hydrolysis at 160° Carried Out for:				
		0 min.	15 min.	30 min.	60 min.	120 min.
Glucose	Strong	Strong	Strong	Strong	Strong	Weak
Fructose	Moderate	Moder- ate	Moder- ate	--	--	--
Sucrose	Possible Trace	Weak	--	--	--	--
Xylose	--	Trace	Weak	Moder- ate	Strong	Very Strong
Xylobiose	--	--	--	Moder- ate	Moder- ate	Weak
Arabinose	--	--	--	Moder- ate	Moder- ate	Weak
Galactose	--	Trace	Weak	Moder- ate	Weak	Weak
Uronic Acids	--	--	--	Weak	Weak	Weak
Mannose	--	--	--	Trace	Trace	Trace

-- means not detected.

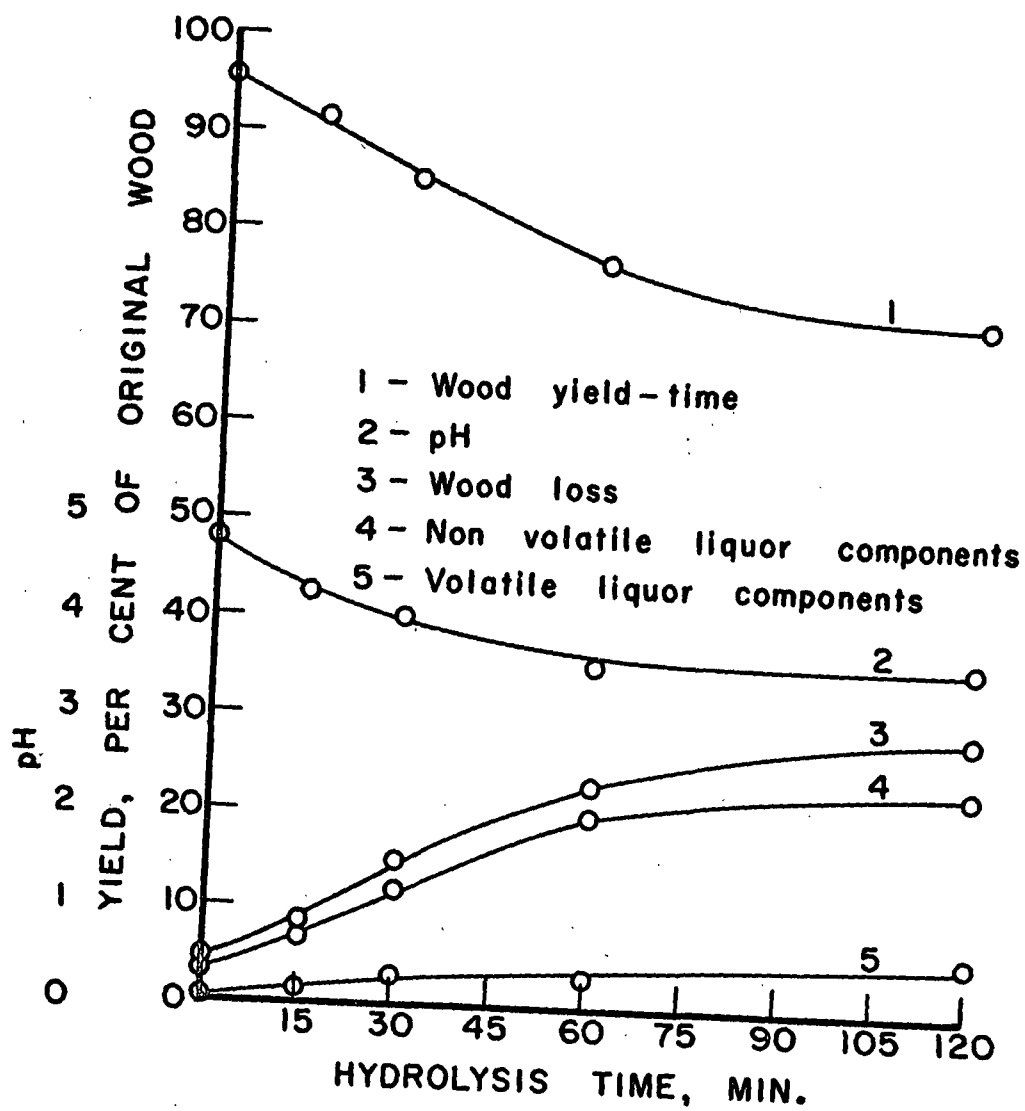


Figure 2. Hydrolyzed Wood Yields and Other Pertinent Data Versus Hydrolysis Time at 160°C.

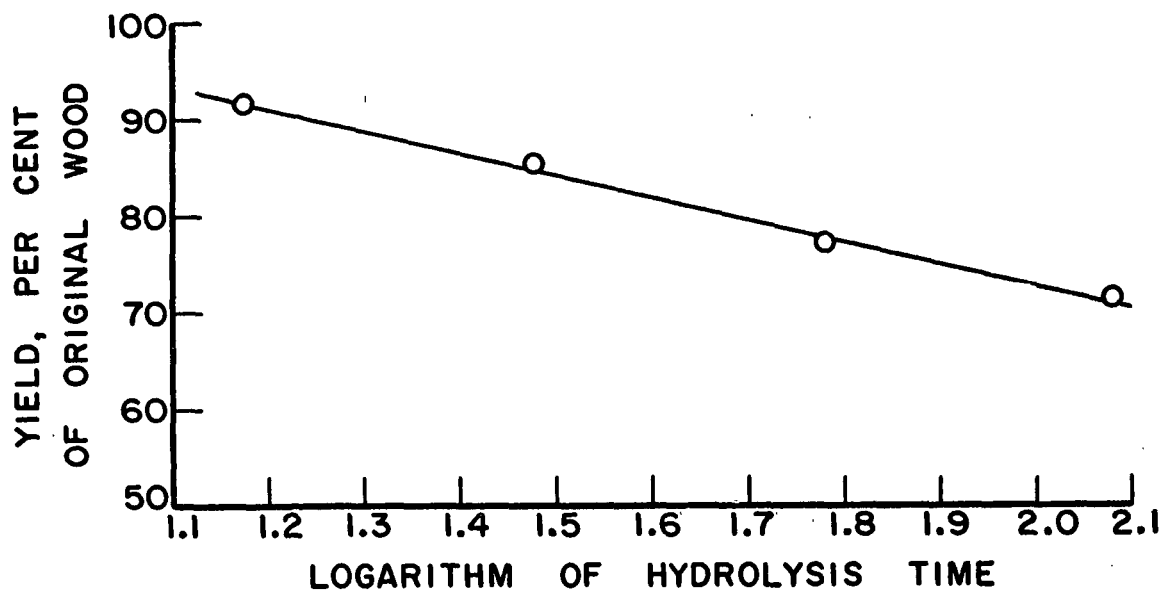


Figure 3. Relationship Between Hydrolyzed Wood Yield and Logarithm of Hydrolysis Time at 160°C.

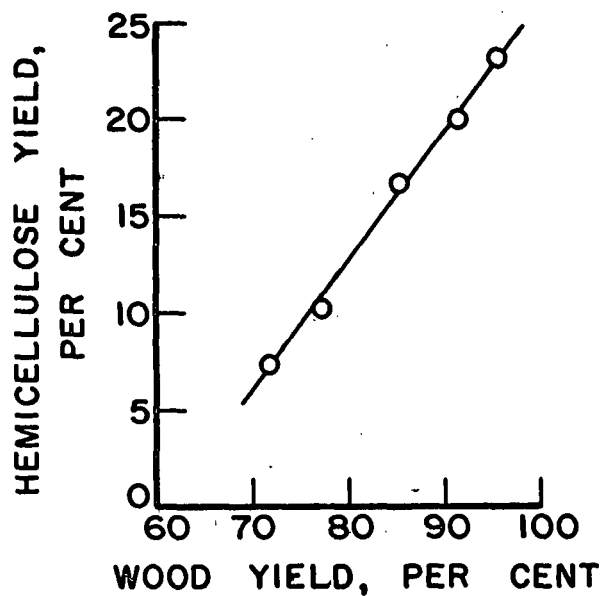


Figure 4. Relationship Between Total Hemicellulose Yield and Hydrolyzed Wood Yield

chromatographically. The polysaccharide from the 0-minute liquor, which originally gave a strong iodine test, on hydrolysis yielded predominantly glucose with traces of xylose and arabinose. Hence, it was presumed to be chiefly starch extracted from the wood by the hot water. The polysaccharide from the 30-minute liquor gave mostly xylose and uronic acids, with a little glucose on acid hydrolysis, and appeared to be chiefly derived from the hemicelluloses.

From Table III it is evident that the alcohol-soluble carbohydrates found in the liquors early in the hydrolysis, chiefly glucose, fructose and sucrose, are also apparent in the cold water extracts of the original wood. Glucose continues to appear prominently in the alcohol-soluble carbohydrates of the liquors throughout the course of the wood hydrolysis, and probably is derived chiefly from the hydrolysis of starch.

As the wood hydrolysis proceeds, however, it is evident that the increase of the alcohol-soluble carbohydrates in the liquors results from hydrolysis of the hemicellulosic polysaccharides of the wood. Xylose and the xylo-oligosaccharides, arabinose, galactose and the uronic acids are found in progressively increasing amounts. Xylose eventually becomes the dominant sugar.

Inasmuch as the polysaccharide isolated from the liquor after 30 minutes of wood hydrolysis is hemicellulosic in nature, the hemicelluloses must be removed from the wood, at least partially, as polymeric fragments. From the progressively increasing amounts of simple sugars of hemicellulosic origin in the liquors, it appears that these polymeric fragments are being further converted into simple sugars by secondary hydrolysis in the liquor.

PROPERTIES OF THE HEMICELLULOSES REMAINING IN THE TISSUE AFTER EACH STAGE OF HYDROLYSIS

YIELDS OF THE HEMICELLULOSE FRACTIONS

The yields of the hemicellulose fractions remaining in the tissue after each stage of hydrolysis are presented in Table IV. The uncorrected data refer to the yields of ash-free hemicelluloses as obtained after completion of the purification sequence by reprecipitation. The corrected yields have been adjusted for the acid-insoluble material obtained on subsequent analyses. These results represent the average of duplicate yield determinations, and the experimental precision is expressed as standard deviation of the duplicates for each polysaccharide fraction.

Summation of the corrected yields of the hemicellulose fractions of unhydrolyzed black gumwood results in a total value of 22.1%. Wise and Pickard (56) found a hemicellulose yield of 22.4% for the sapwood of blended samples of black gumwood.

In Figure 4 the close correlation between loss of hemicellulose from the wood and decrease of wood yield during hydrolysis is illustrated. About 55% of the total material removed from black gum is hemicellulose. Presumably the rest is a complex mixture of lignin, extractives, acetic acid and other reaction products.

CHEMICAL ANALYSIS OF THE FRACTIONS

The results of the analyses of the 5 and 16% hemicelluloses are listed in Tables V and VI, respectively. The percentages of xylan, which was the

TABLE IV

YIELDS OF THE HEMICELLULOSE FRACTIONS¹ FOUND IN THE
WOODY RESIDUES AFTER EACH HYDROLYTIC STAGE

Hydrol. Time	Hemicellulose Yields						
	5% Fraction		16% Fraction ²		<u>C</u> Fraction ³	Total	
	Uncorr.,	Corr., ²	Uncorr.,	Corr.,		Uncorr.,	Corr., ²
	%	%	%	%	%	%	%
Orig. wood	15.7	15.2	4.6	4.6	2.5	22.8	22.1
0 min.	17.7	16.4	5.1	4.9	1.8	24.6	23.1
15 min.	17.3	16.3	3.8	3.7	—	21.1	20.0
30 min.	15.0	13.6	3.2	3.1	—	18.2	16.7
60 min.	9.6	8.0	2.4	2.2	—	12.0	10.2
120 min.	8.1	5.5	2.1	1.8	—	10.2	7.3

-
- ¹ Percentages are calculated as ash-free, oven-dry yields on the original wood basis.
 - ² Corrected for acid-insoluble, noncarbohydrate component.
 - ³ The polysaccharide fraction obtained during the last alkaline extraction with 16% potassium hydroxide in the procedure for preparation of the alkali-resistant cellulose. For the hydrolysis stages, 15-120 min., the yield was insignificant.
- Standard deviations — 5% hemicelluloses 0.52
 16% hemicelluloses 0.17
C fractions³ 0.22

principal component of all the fractions analyzed, were adjusted for loss through decomposition during the acidic hydrolysis of the polysaccharides to their constituent sugars. This was estimated empirically as a 10% loss by subjecting pure xylose to equivalent hydrolysis conditions. The analyses represent the average of duplicate determinations, except when otherwise specified.

The 'insolubles' listed in the tables represent those portions remaining undissolved in the hydrolyzing acid. Because this residue does not give typical lignin tests, these fractions are presumably due chiefly to decomposition of carbohydrates under the extreme conditions of the wood hydrolysis, and to condensation or polymerization of reactive liquor components. The significance of this component, with regard to the polysaccharide yields and molecular weights, is discussed later.

Several factors may contribute to the relatively low summative analyses. The chief of these is the retention of significant amounts of xylose in the form of aldobiuronic acids, which are very resistant to hydrolysis. Aldobiuronic acids are not appreciably hydrolyzed in boiling, dilute acids unless conditions are so severe that considerable degradation of the carbohydrates will occur (6). Since three to four acid spots were found on the paper chromatograms of these hydrolyzates, it is probable that significant quantities of these uronic acid derivatives are present. Wise and Pickard (57) found chromatographic evidence for 2- α (4-O-Me-glucuronosyl) D-xylose in the hydrolyzate of black gum, and so it is likely, in view of the high percentages of uronic anhydride encountered, that a

TABLE V

ANALYSES OF THE 5% HEMICELLULOSES

Basis: Percentage Oven-dry, Ash-Free Hemicellulose

Component	Hemicel- lulose of Original Wood	Hemicellulose Isolated After Hydrolyzing at 160°C. for:				
		0 min.	15 min.	30 min.	60 min.	120 min.
Uronic anhydride, % ¹	16.9	17.0	14.8	14.2	12.3	11.6
Xylan, % ²	65.7	59.0	64.0	60.0	55.8	44.0
Glucan, %	1.7	2.8	2.3	1.7	0.8	1.2
Galactan, %	0.6	1.0	1.2	0.7	0.9	
Mannan, %	--	--	--	0.4	--	0.5
Araban, %	0.6	--	--	--	--	--
Rhamnan, %	1.0	--	--	--	--	--
Insolubles, ³ %	3.2	7.2	5.6	9.7	16.7	32.3
Summation, %	89.7	87.0	87.9	86.7	86.5	89.6

¹ See footnote 1, Table VI

² See footnote 2, Table VI

³ Single determinations.

TABLE VI

ANALYSES OF THE 16% HEMICELLULOSES

Basis: Percentage Oven-dry, Ash-Free Hemicellulose

Component	Hemicel- lulose of Original Wood	Hemicellulose Isolated After Hydrolyzing at 160°C. for:				
		0 min.	15 min.	30 min.	60 min.	120 min.
Uronic anhydride, % ¹	15.2	12.5	10.2	10.7	8.3 ⁵	7.6 ⁵
Xylan, % ²	65.0	64.0	61.5	70.4	60.0	60.8
Glucan + Galactan, % ³	4.7	4.5	4.7	6.3	5.2	4.9
Mannan, % ⁴	4.7	3.4	5.0	6.2	6.1	6.2
Insolubles, % ⁵	5.5	3.5	2.3	3.5	9.8	12.3
Summation, %	95.1	87.9	83.7 ⁶	97.1	89.4	91.8

1. Standard deviation--0.29.

2. Standard deviation--1.91.

3. Standard deviation--0.13.

4. Standard deviation--0.26.

5. Single determinations.

6. Hydrolyzate may have been slightly decomposed in concentrator.

significant amount of xylose remains unaccounted for in the chromatographic analysis.

Furthermore, there is no satisfactory method of determining noncarbohydrate materials soluble in the acid hydrolyzate. The ultraviolet absorption spectra of hemicellulose hydrolyzates show a furfural peak and phenolic absorption. Uronic acids are frequently present as O-Me derivatives and there is no adequate way of evaluating this degree of etherification in the presence of small amounts of lignin. Finally, only the xylan has been corrected for decomposition of xylose during hemicellulose hydrolysis. Admittedly this correction is only an approximate one. Any or all of these factors might contribute to the low summations.

From the hemicellulose analyses the xylan and uronic anhydride contents of the wood were evaluated as a function of the degree of wood hydrolysis, in Table VII. All percentages are based on the weight of original wood, although they are allocated to the specific polysaccharide fraction from which they are derived. As shown subsequently in this paper, a small amount of xylan was found in the alkali-resistant celluloses. This residual xylan is also included in summation of the xylan content of each hydrolyzed wood. The xylan to uronic acid ratio in the polysaccharide fractions, as well as in the woody residue are also shown.

Of the several stages of hydrolysis presented in Table VII, the yield of the additional C-fraction of hemicellulose, obtained during the last extraction step in the preparation of the alkali-resistant cellulose, was significant in the zero-minute stage only. Lacking the carbohydrate

TABLE VII

CONTENTS AND RELATIVE PROPORTIONS OF XYLAN
AND URONIC ANHYDRIDE IN THE HYDROLYZED WOOD

Hydrolysis Time, min.	Basis: Percent, Oven-dry Original Wood						Total	
	5% Hemicellulose	16% Hemicellulose ²	A. R. C. ³	Xylan, % U.A., % Xylan/U.A.	Xylan, % U.A., % Xylan/U.A.	Xylan, % U.A., % Xylan/U.A.		
0	10.5	3.0	3.5	4.4	0.8	6.0	1.3	16.2
15	11.1	2.6	4.2	2.3	0.4	5.7	0.8	14.2
30	9.0	2.1	4.3	2.2	0.3	7.3	0.7	11.9
60	5.4	1.2	4.5	1.4	0.2	7.0	0.6	7.4
120	3.6	0.9	3.8	1.3	0.2	8.0	0.5	5.4
								1.1
								4.8

¹ Uronic anhydride.

² Hemicellulose C included in 16% fraction (see text).

³ Alkali-resistant cellulose.

composition of this fraction, it was assumed that the proportions of xylan and uronic anhydride existed as those found in the 16% fraction at this stage.

In Figures 5-7, the course of the removal of the hemicelluloses and their principal components from the wood are shown as a function of hydrolysis time. The progress of the dissolution of the hemicelluloses is shown in terms of the accessible (5%) and resistant (16% plus C) fractions in Figure 5. Although the rate of removal of the sum of the hemicellulose fractions, based on the weight of original wood, is essentially constant over the first 60 minutes of reaction, the attack on the resistant fractions is proportionately much greater than on the 5% fraction. Inasmuch as the gross carbohydrate composition of the hemicelluloses is not affected markedly by the hydrolysis, the removal rate of xylan from the wood, in Figure 6, closely parallels that of the total polyose.

The cumulative removal of the hemicelluloses is expressed as a function of hydrolysis time in Figure 7. Apparently, 60% of the hemicellulose content of black gumwood is readily removed by the hydrolysis treatment, but the attack on the last 40% is much slower.

CHAIN-LENGTH DEGRADATION OF THE HEMICELLULOSES DURING GRADED HYDROLYSIS

The intrinsic viscosities and number-average degrees of polymerization of all the 5 and 16%-hemicellulose fractions are shown in Table VIII. These resulted from the best extrapolation of duplicate sets of reduced viscosity data for each purified fraction, as given in Figures 8 and 9. In the case

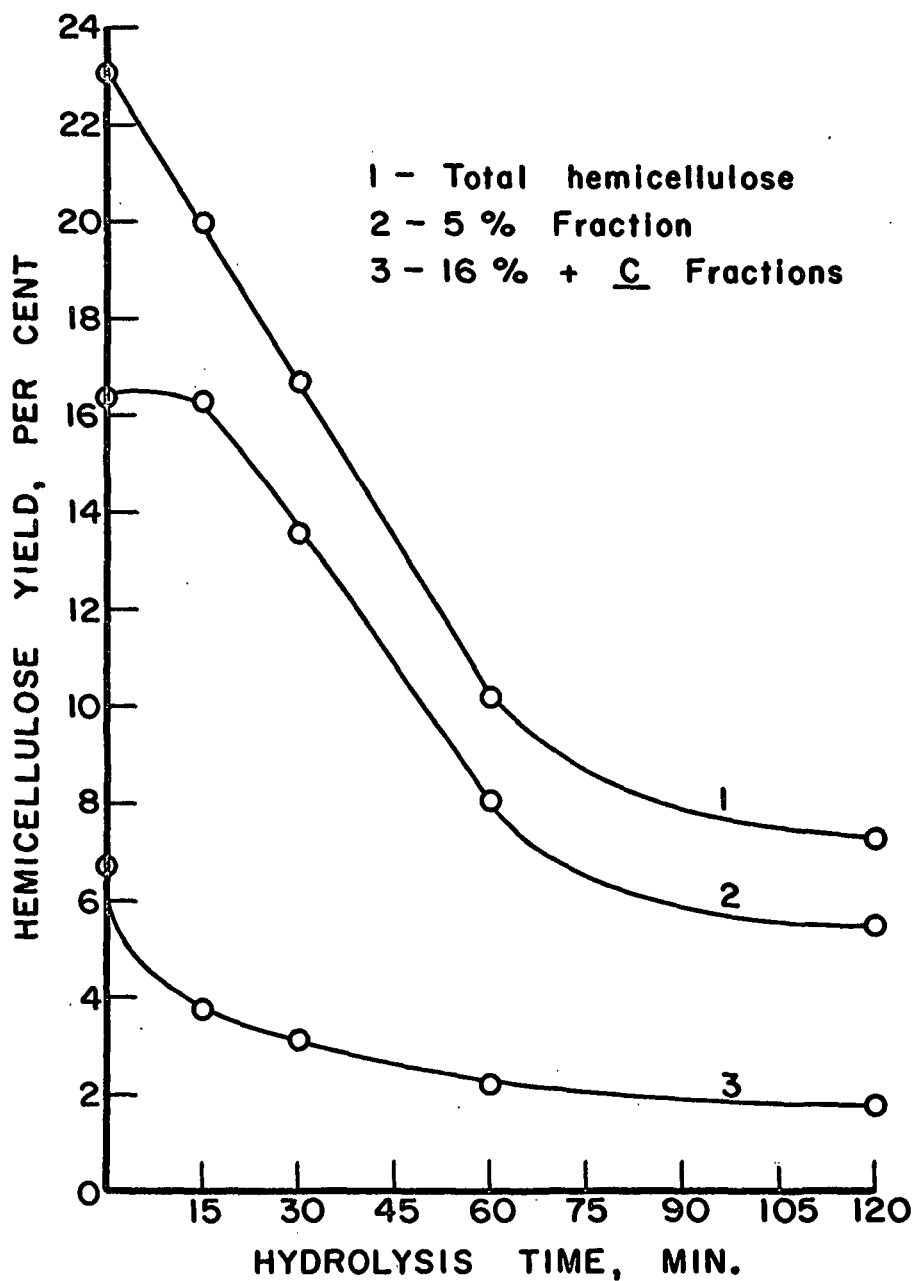


Figure 5. Yields of the Hemicelluloses (Original Wood Basis) Remaining in the Tissue Versus Hydrolysis Time at 160°C.

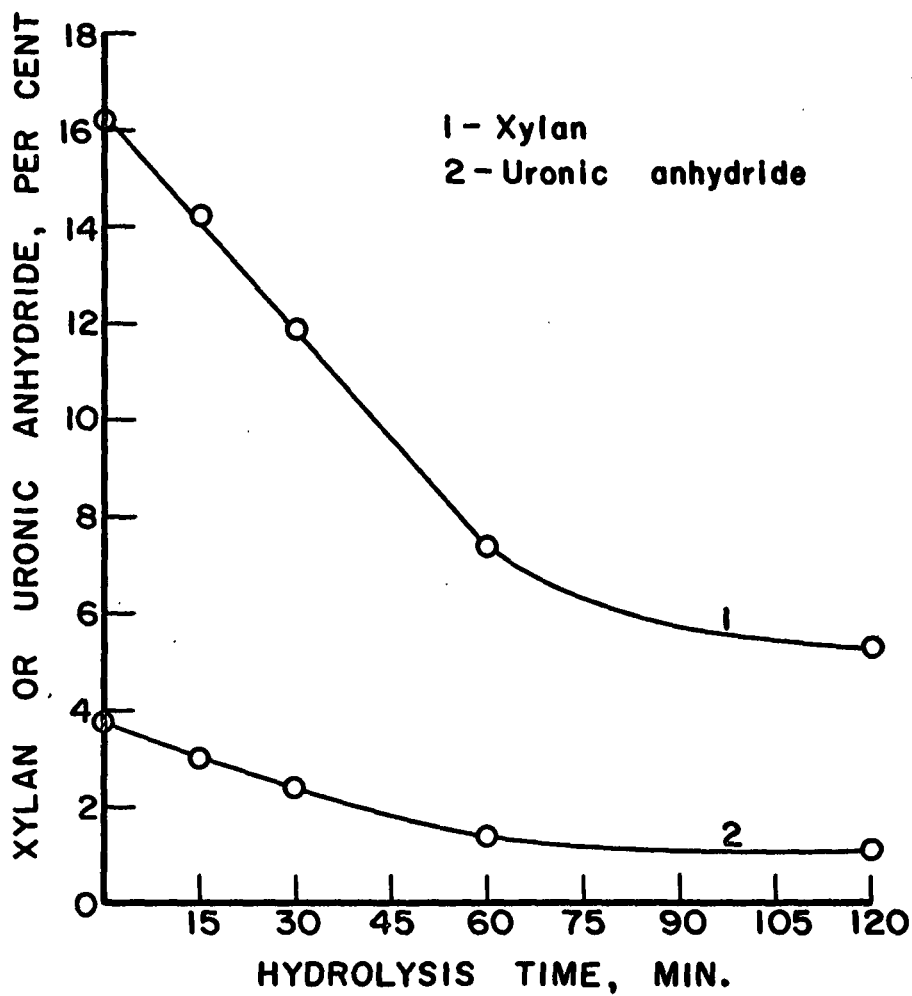


Figure 6. Xylan and Uronic Anhydride Contents (Original Wood Basis) Hydrolyzed Wood Versus Hydrolysis Time at 160°C.

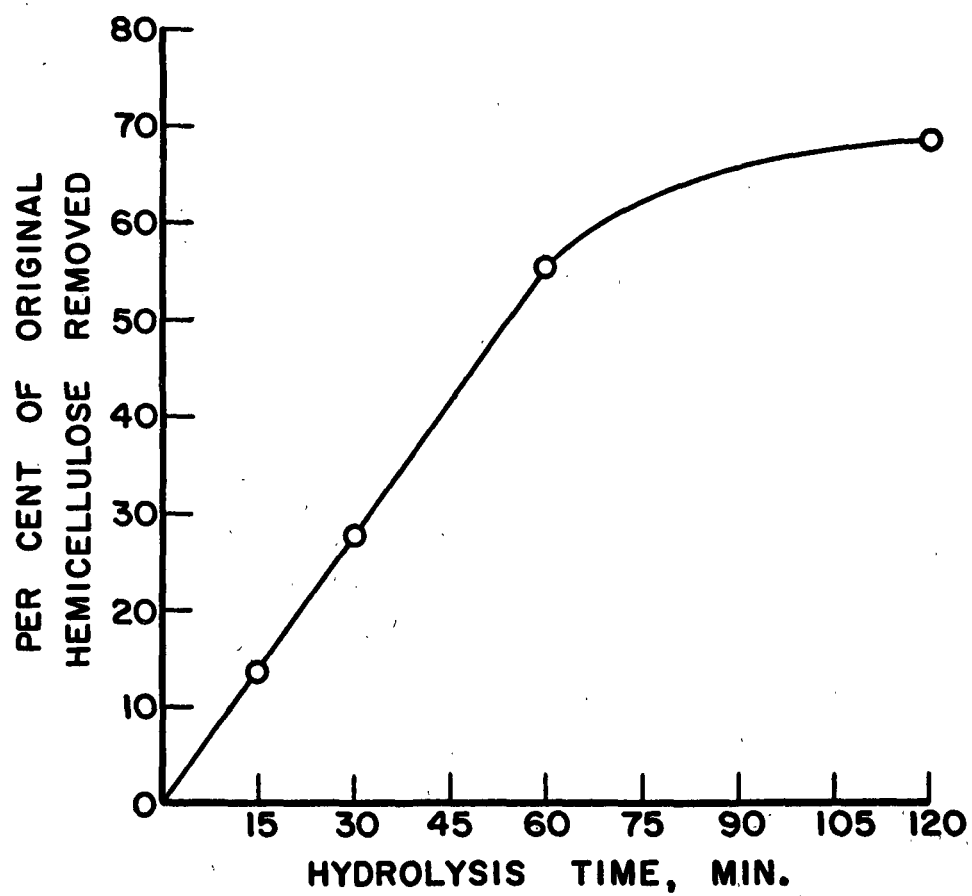


Figure 7. Cumulative Removal of the Hemicelluloses Versus Time of Hydrolysis at 160°C.

of the 5% polysaccharide obtained from 15 minutes of hydrolysis, the intrinsic viscosity before and after the last reprecipitation in the purification sequence was determined so as to evaluate its effect on the polymer D.P. A 5% increase was observed due to the additional purification.

Column 5 of Table VIII contains number-average D.P.'s representative of the total hemicellulose remaining in the woody residue after each stage of hydrolysis. These values were calculated from the chain lengths of the respective 5 and 16% fractions by Equation (8),

$$D.P._t = Y_t / (Y_{5\%} D.P._{5\%} + Y_{16\%} D.P._{16\%}), \quad (8)$$

where t refers to the cumulative hemicellulose fractions, and Y refers to yield. Equation (8) is derived from the definition of number average molecular weight (\bar{M}_n),

$$\bar{M}_n = \sum_i n_i M_i / \sum_i n_i, \quad (9)$$

where n_i is the number of moles of polymer having molecular weight M_i and \sum_i represents summation of all polymeric units.

There was no way of estimating the true molecular weights of the hemicellulose-C fractions, which were obtained after chloriting the residues from the 16% extractions of the original and zero-minute hydrolyzed woods. Inasmuch as the yields were small and could be classed with the more alkali-resistant hemicelluloses of the woody residues, the C fractions were assumed to have the same D.P. as the respective 16% fractions in calculating the average chain lengths of the cumulative fractions.

Many of the fractions retained appreciable amounts of acid-insoluble material. Inasmuch as this material was nonpolysaccharidic, its influence

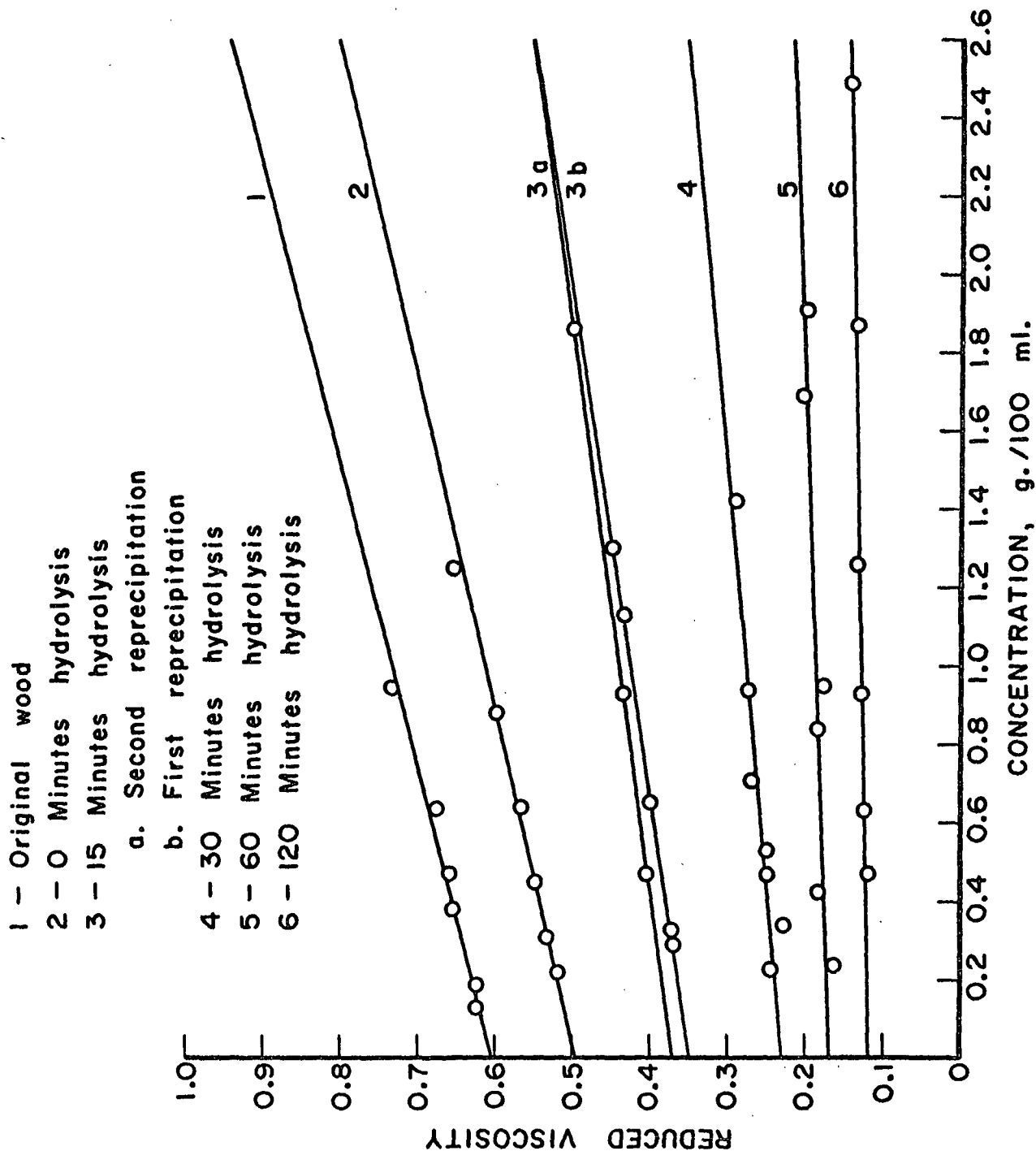


Figure 8. Extrapolation of the Reduced Viscosities of the 5% Hemicelluloses to Zero Concentration

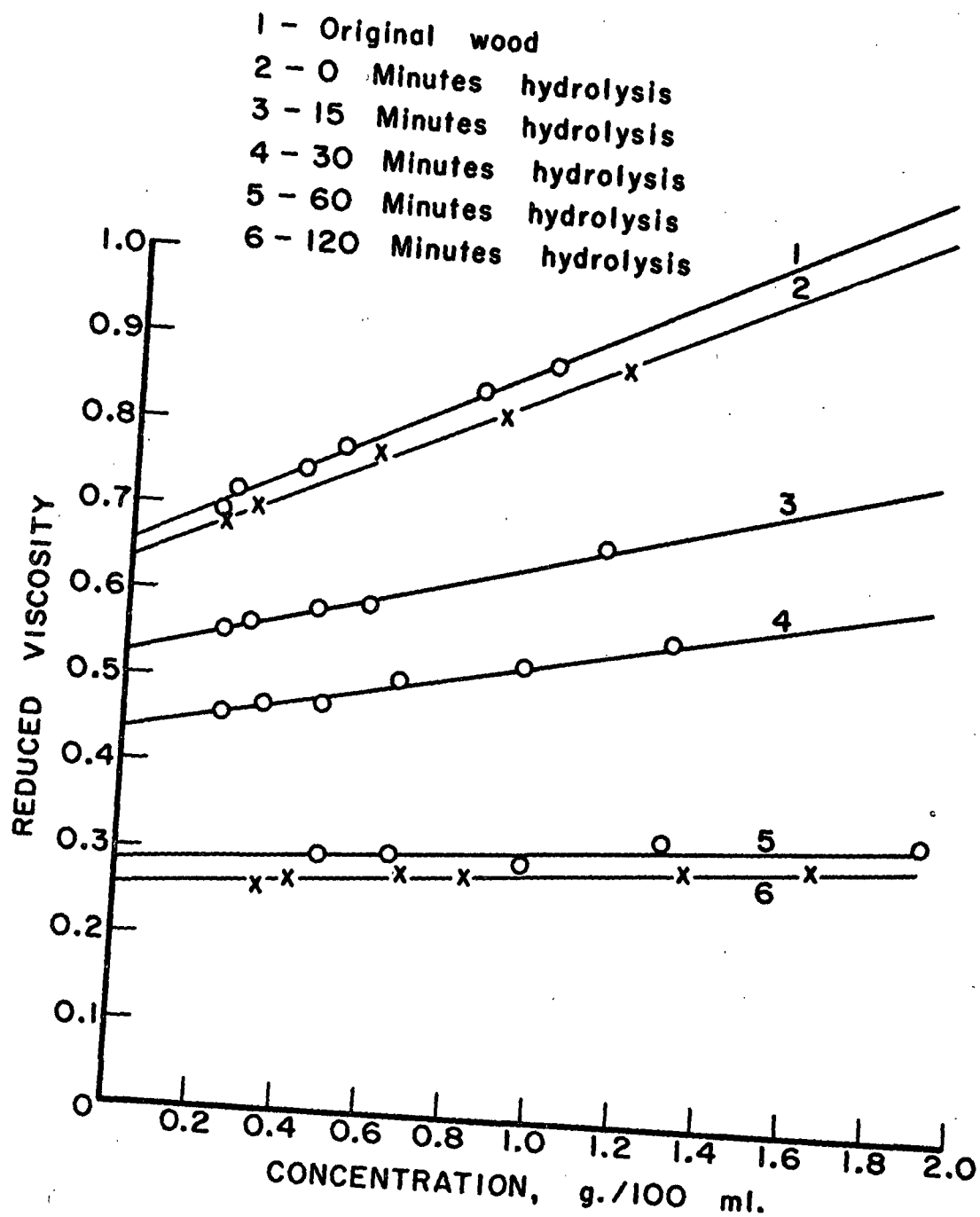


Figure 9. Extrapolation of the Reduced Viscosities of the 16% Hemicelluloses to Zero Concentration

TABLE VIII

INTRINSIC VISCOSITIES AND NUMBER-AVERAGE
D.P.'s FOR THE HEMICELLULOSES*

Hydrol. Time, min.	5% Fraction		16% Fraction		Total Hemicellulose D.P.
	[η] D.P.		[η] D.P.		
Orig. wood	0.61	139	0.65	148	141
0	0.50	114	0.63	143	121
15	0.37	84	0.52	118	89
30	0.23	53	0.43	98	58
60	0.17	39	0.29	66	43
120	0.12	29	0.26	59	32

*Calculated as pentosan.

TABLE IX

NUMBER-AVERAGE D.P.'s OF THE HEMICELLULOSES

Hydrol. Time, min.	5% Fraction		16% Fraction		Total Hemicellulose	
	D.P.	D.P. ¹	D.P.	D.P. ¹	D.P.	D.P. ¹
	Uncorr.	Corr.	Uncorr.	Corr.	Uncorr.	Corr.
Orig. wood	139	141	148	158	141	145
0	114	120	143	151	121	128
15	84	88	118	121	89	92
30	53	59	98	103	58	63
60	39	45	66	68	43	49
120	27	40	59	64	32	44

¹ Corrected for acid-insoluble fraction of the hemicellulose.

on the molecular weights of the polyose fractions was estimated. The acid insolubles were assumed to be present as physical contaminants making no appreciable contribution to the solution viscosities of the hemicelluloses. The results of these calculations, compared with the original values, are shown in Table IX.

Evidently the adjustments in the chain-length values resulting from these corrections are not very significant, with the possible exception of the 5% hemicelluloses obtained in the 120-minute hydrolysis stage. Usually the corrections fall within the limits of experimental accuracy. Since the assumption was made that the nonpolysaccharidic contaminants did not contribute to the viscosity behavior of the hemicelluloses, the corrected D.P.'s represent maximum chain-length values.

These results are expressed graphically as a function of hydrolysis time in Figure 10. Evidently a very rapid polymeric degradation of either fraction begins almost from the start. Since some hemicellulose is being continuously removed from the wood, these data describe only the heterogeneous phase of the hydrolysis.

PROPERTIES OF THE ALKALI-RESISTANT CELLULOSES DURING GRADED HYDROLYSIS

YIELDS AND CHAIN-LENGTH DEGRADATION

The yields and average chain lengths of the alkali-resistant celluloses from the wood at each stage of hydrolysis are listed in Table X. The yields are presented on the original wood basis and all data represent the average of duplicate determinations.

The cellulose isolated from unhydrolyzed wood was severely degraded during its isolation. This was indicated by subsequent viscosity measurements. The possible influence of the mechanical action received by the original wood as a source of the degradation was investigated. Hence, the yields and D.P.'s of alkali-resistant celluloses, prepared through direct chloriting and extracting wood shavings, on the one hand, and 30 to 80-mesh wood meal on the other are also recorded in Table X.

The intrinsic viscosities reported in Table X were calculated from the reduced viscosities according to Equation (6). Duplicate determinations showed an average deviation from the mean of less than 1%. The agreement of the data is shown in Figure 11, in which the lines joining the calculated intrinsic viscosity with the observed reduced viscosities for each step in the hydrolysis have a slope of 0.133 [7]. The only exception to this pattern was shown by the cellulose prepared directly from wood shavings, in which the calculated extrapolation, based on K' equal to 0.133 did not fit the data. A four-point extrapolation gave a K' value of 0.155, possibly due to a spurious effect caused by the difficult solution of fiber clumps in this sample.

The hydrolysis causes only a slight reduction in the cellulose yield. The yields are affected somewhat by the method of isolation, as in the case of the original wood. However, conversion of shavings to wood meal has little effect on the cellulose D.P.

The chain-length degradation of the cellulose is given as a function of hydrolysis time in Figure 12, and compared with the hemicellulose

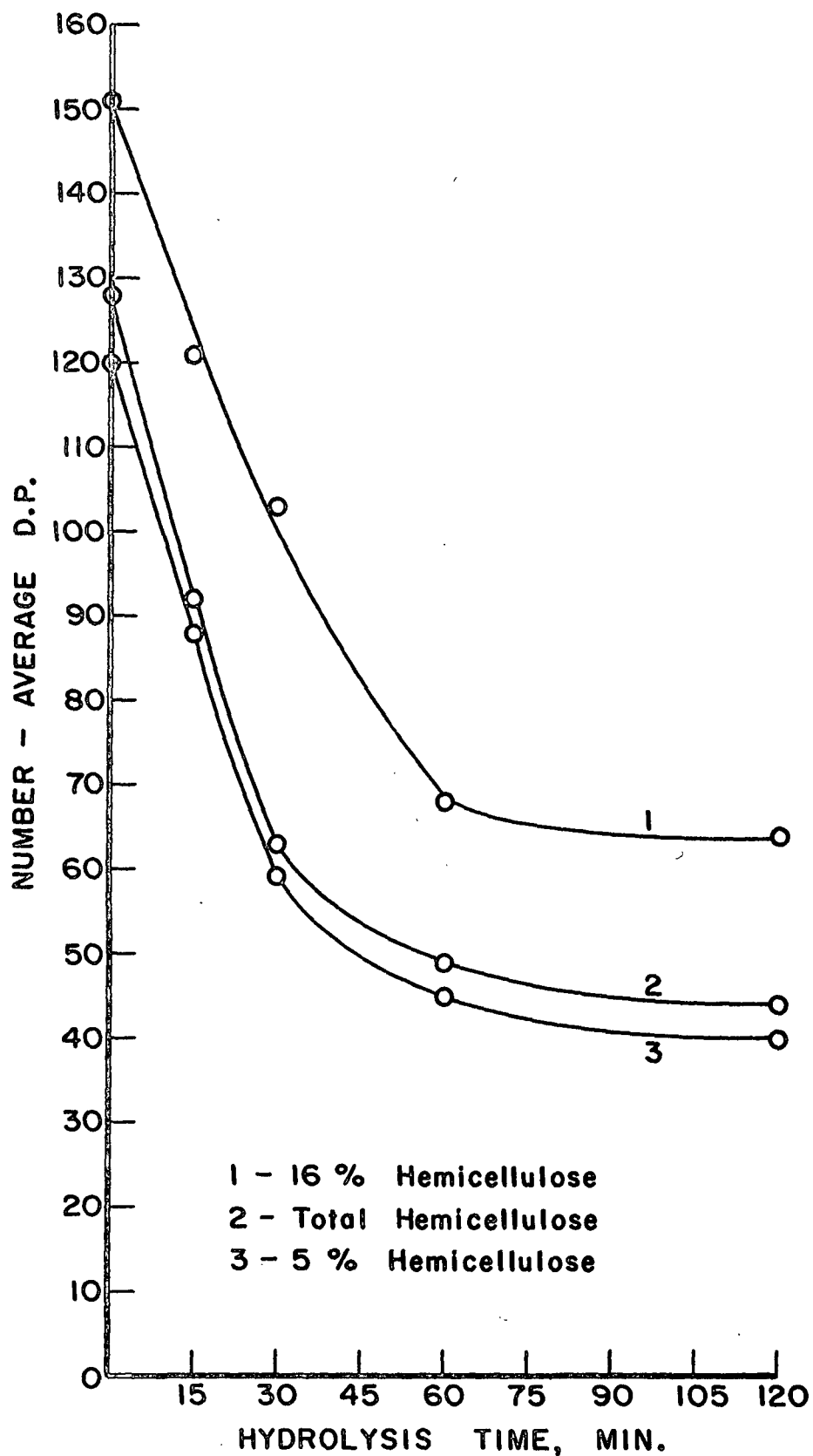


Figure 10. Average Chain-Length Degradation of the Hemicelluloses During Aqueous Hydrolysis

TABLE X

YIELDS AND DEGREES OF POLYMERIZATION
OF THE ALKALI-RESISTANT CELLULOSES

Hydrolysis Time, min.	Yield, ⁵ %	Intrinsic Viscosity	D.P. ⁴
Original wood shavings	47.2 ^{2,6}	10.8	1850
Original wood meal	46.6 ^{3,6}	10.4	1770
0	45.1 ¹	9.4	1600
15	44.5 ¹	8.1	1370
30	43.3 ¹	6.9	1175
60	43.6 ¹	6.5	1100
120	43.7 ¹	5.9	1000

-
1. Prepared by chlorine-ethanolamine procedure, 5 and 16%-KOH extractions, 1 hr. chloriting, and 16% KOH extraction.
 2. Prepared by chloriting pre-extracted wood shavings 4 times at 70°C. followed by 5 and 16%-KOH extractions.
 3. Prepared by chloriting pre-extracted wood meal (30-80 mesh) 3 times at 70°C., followed by 5 and 16%-KOH extractions.
 4. Calculated as the products: $[\eta] \times 170$.
 5. Percent based on oven-dry, original wood. Yields represent the average of duplicate determinations with standard deviation equal to 0.1.
 6. Single determinations.

degradation in Figure 13. The average degree of polymerization of the cellulose is considerably reduced during the hydrolysis of the wood. As in the case of the hemicelluloses, cellulose hydrolysis is more rapid during the first hour; but the depolymerization is less marked than in the case of the hemicelluloses.

ANALYSES OF REPRESENTATIVE ALKALI-RESISTANT CELLULOSES

The analyses for the constituent sugars of the alkali-resistant celluloses from the 0, 30 and 120-minute hydrolysis stages are tabulated in Table XI. Since the only sugars other than glucose appearing in the hydrolyzate were mannose and xylose, glucose was obtained by difference. The data, which represent the average of duplicate determinations, are presented both on the basis of the cellulose and of the original wood.

TABLE XI

ANALYSES OF SELECTED ALKALI-RESISTANT CELLULOSES FROM HYDROLYZED WOODS

Hydrol. Time, min.	Based on Cellulose,			Based on Wood,		
	Glucan ²	% Mannan ¹	Xylan ¹	Glucan ²	% Mannan ¹	Xylan ¹
0	92.6	4.6	2.8	41.8	2.1	1.3
30	94.2	4.3	1.5	40.7	1.9	0.7
120	95.7	3.1	1.2	41.7	1.4	0.5

¹ Standard deviation of xylan and mannan analyses = 0.34.
² Obtained by difference.

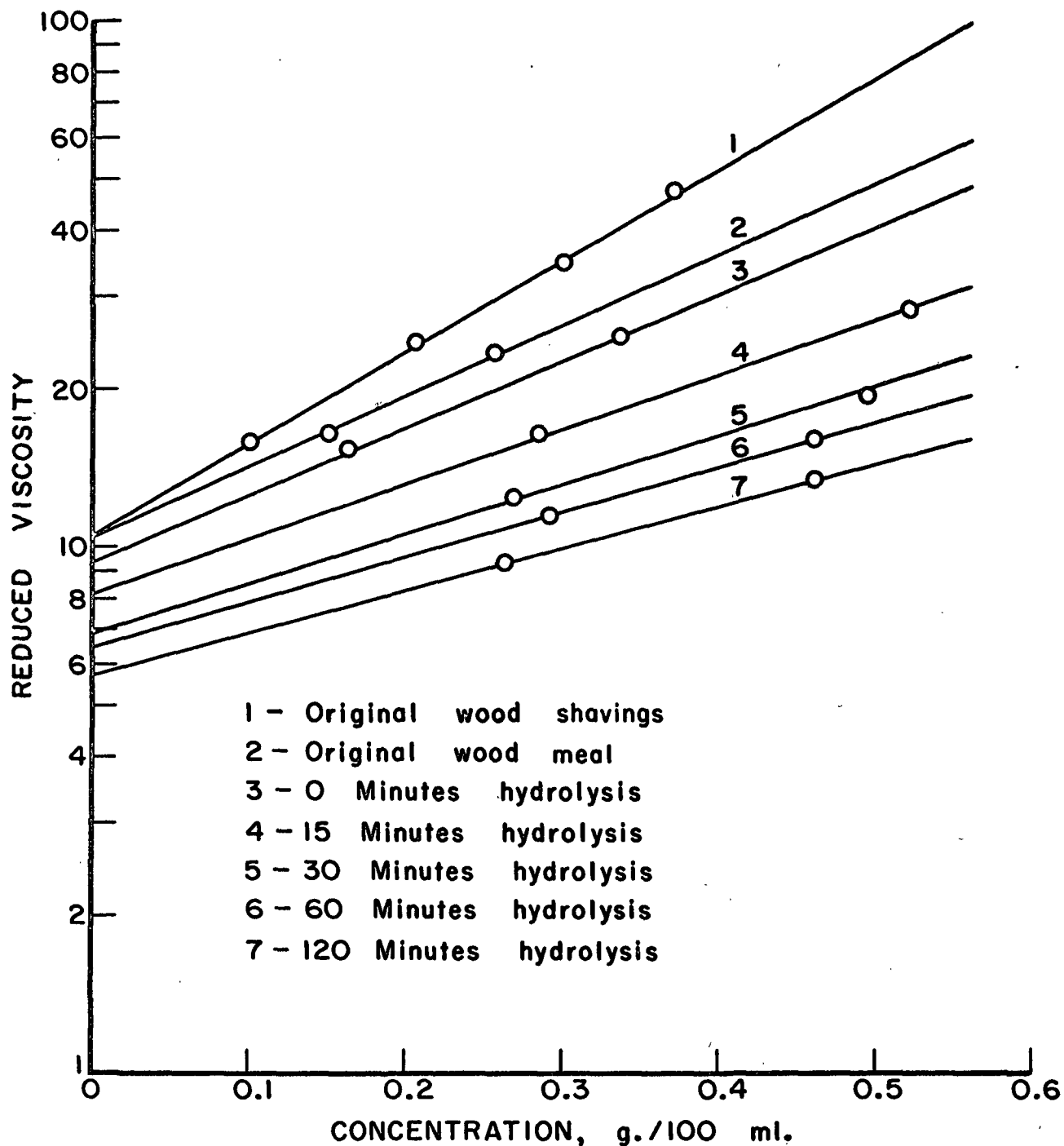


Figure 11. Extrapolation of the Reduced Viscosities of the Alkali-Resistant Celluloses to Zero Concentration

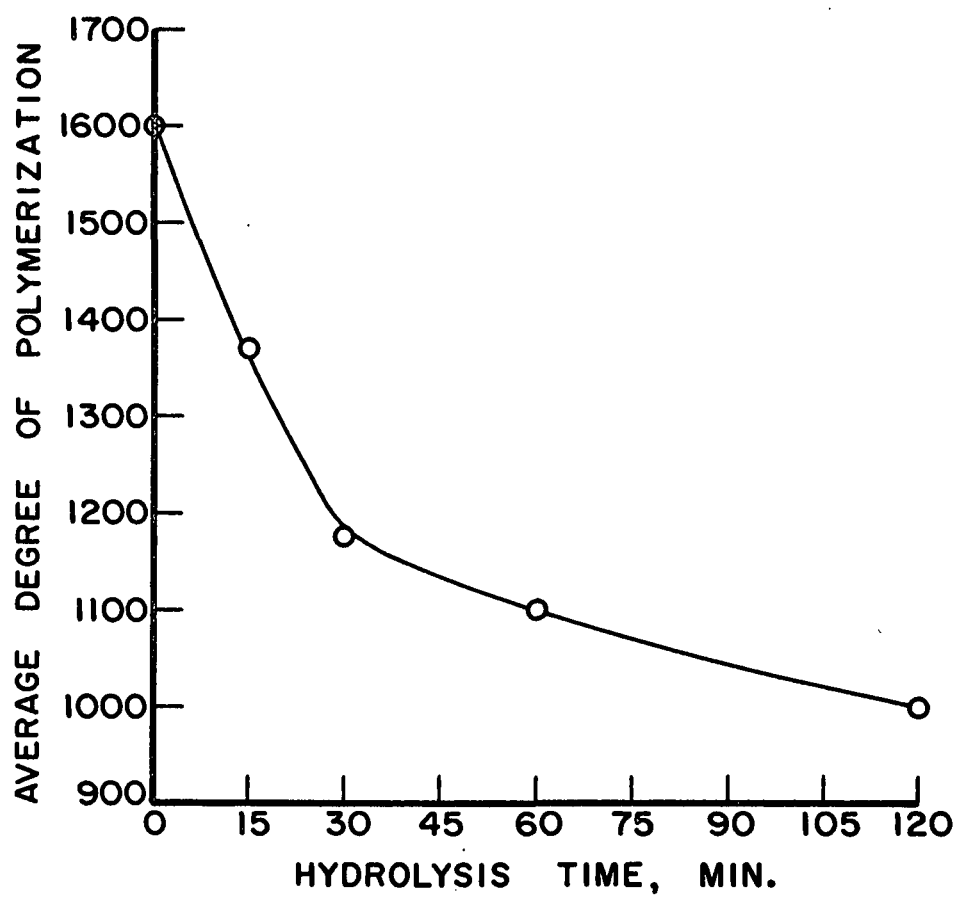


Figure 12. Average Chain-Length Degradation of the Alkali-Resistant Cellulose During Aqueous Hydrolysis at 160°C.

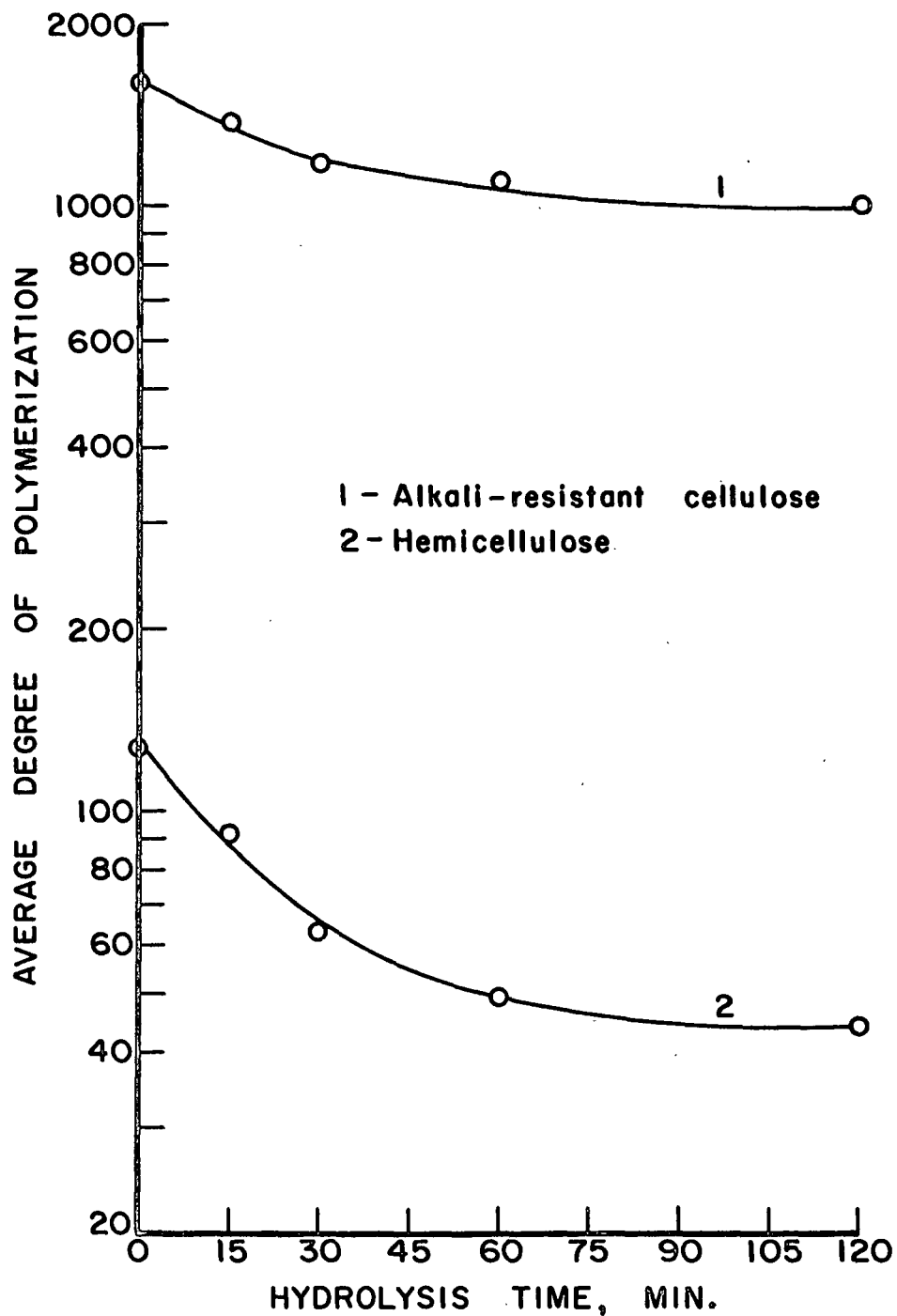


Figure 13. Comparison of the Cellulose and Hemicellulose Chain-Length Degradations During Aqueous Hydrolysis at 160°C.

X-RAY DIFFRACTION SPECTRA

From the x-ray diffraction spectra of the alkali-resistant celluloses from the 0 and 120-minute hydrolysis stages, it appeared that the more highly hydrolyzed sample gave a slightly sharper crystalline pattern. Presumably, however, the intense mercerizing treatments received by the celluloses during the hemicellulose extractions with 16% potassium hydroxide have masked the true differences. Hence, these experiments were inconclusive, and the diffraction spectra are not included in the present thesis.

DISCUSSION OF RESULTS

The experimental conditions used in the present wood hydrolysis were unique. Due to the short time required to bring the system to operating temperature and the controls maintained during the reactions, the results are, for all practical purposes, representative of hydrolysis at 160°C. for the time intervals specified.

As shown in Figure 3, the yield of wood is a linear function of the logarithm of hydrolysis time over a two-hour period at 160°C. During this time the wood yield is reduced by nearly 30%. Of the material removed, about 55% consists of hemicellulosic polysaccharides; the remainder is a complex mixture of extractives, lignin and decomposition products of the wood components.

The hydrolysis may be described as a simultaneous degradation of both the cellulosic and hemicellulosic polysaccharides, and is selective in degree only. The relatively slight loss of the "cellulose" yield is chiefly due to the removal of xylose and mannose units during the course of hydrolysis, as indicated in Table XI.

About 70% of the original hemicellulose content of the wood is removed within 2 hours. In the very early stages, the hemicelluloses most resistant to alkaline extraction are rapidly converted to a more accessible form. This is strikingly illustrated by the 45% reduction in the summative yields of the 16% and C fractions during the first 15 minutes of reaction, while the corresponding drop in the yield of the 5% fraction is less than 1%. The

high initial loss in 16% and hemicellulose C fractions appears to be due to a cleavage of these higher polymers into hemicellulose fragments that fall in the range of the 5% hemicelluloses. Thus, while polymers of the latter type are removed, others are actually being formed. Hence the drop in the original 5% hemicellulose content of the wood (during this period) is probably much greater than the 1% actually observed. The new 5% hemicellulose formation almost balances that which was lost in the hydrolysis.

Despite this rapid conversion of hemicellulosic polysaccharide to a readily extractable form, the removal rate of the polyoses from the wood remains essentially constant within the first hour. This behavior is characteristic of a zero-order reaction, and of surface reactions in which rate of diffusion is the controlling factor in the kinetics. However, it is doubtful that any such simple mechanism can completely represent the complex physicochemical phenomena involved in this heterogeneous system. The removal rate falls off rapidly during the second hour and thus fails to follow any simple kinetic pattern.

Further insight into the nature of the hydrolysis can be obtained by evaluating the rates of solution of the polysaccharides in terms of the amount available in the wood at any given time. In Table XII, the 2-hour study has been broken down arbitrarily into eight, 15-minute intervals. The function, $\Delta C / C \times 100$ has been evaluated for the xylan and total hemicellulose contents of the wood for each 15-minute interval. In this analysis, ΔC represents the drop in concentration of the component in the

wood over the designated interval, and \bar{C} , the average content of the component in the wood over the same interval. The function, $\Delta\bar{C}/\bar{C} \times 100$ is essentially equal to $K \times 100$, where K is the first-order reaction rate constant in reciprocal 15-minute units.

The values of $\Delta\bar{C}$ and \bar{C} of the hemicelluloses and xylan for each of the eight hydrolysis intervals were read from the respective curves in Figures 5 and 6.

TABLE XII

REMOVAL RATES OF THE HEMICELLULOSES AND
XYLAN FROM WOOD DURING HYDROLYSIS

Hydrolysis Interval, min.	$\Delta\bar{C}/\bar{C} \times 100^1$	
	Total Hemi- cellulose	Xylan
0-15	14.3	14.6
15-30	18.0	17.0
30-45	21.2	20.6
45-60	27.7	25.6
60-75	14.7	14.7
75-90	9.5	11.7
90-105	6.4	6.4
105-120	2.7	1.9

¹ $\Delta\bar{C}/\bar{C} \times 100$ represents the percentage change in the average amount of the component available in the hydrolyzed wood over the given time interval.

It is obvious that the removal rate of the hemicelluloses does not follow a first-order reaction. The rate of solution, based on the amount of polysaccharide available at any given time, increases steadily throughout the first hour. During the fourth 15-minute interval the rate is nearly double that of the initial value. This is then followed by a sudden drop, and in the final period, it is less than 20% of the initial rate.

Thus, the removal rate of the hemicelluloses from the wood during hydrolysis is not related solely to the amount present at any given time. The simultaneous reduction in average chain length of the polysaccharides appears to be a primary contributive factor. Within 30 minutes at 160°C., the average D.P. of the hemicelluloses in the wood is reduced by 50%; after 60 minutes, by 65%.

This hydrolytic decrease in polymolecularity is concomitant with an increase in the number and solubility of the polysaccharide chains in the tissue. Despite the amount of hemicellulose removed from the wood, the number of polysaccharide molecules present in the fibrous residue has actually increased by about 40% after a hydrolysis of 30 minutes, as compared with 0 time, based on calculations from the corrected data in Tables IV and IX.

Furthermore, the hemicellulose fractions were not markedly changed in gross carbohydrate composition during the course of hydrolysis. The consistency in the relative proportions of sugars and uronic acids precludes the likelihood that selective solution of major constituents contributes significantly to the rate of polysaccharide removal.

The sharp break in the removal rate during the second hour of hydrolysis may be due to a number of factors. Lange and Asunmaa (58) have reported that the hemicelluloses of wood are highly concentrated at the outer surface of the fiber wall, and decrease in amount in approaching the lumen. Assuming that the most readily dissolved polysaccharides are located near the surface, the final residual polyoses would be well distributed throughout the secondary wall of the fiber. Thus, despite their potentially greater solubility due to their shorter chain length, they must diffuse through the retaining structure of the fiber wall.

Another interesting possible explanation of this behavior derives from the progressively increasing amounts of the various hydrolytic degradation products closely associated with the hemicelluloses. These noncarbohydrates, which are manifested as acid insolubles, may significantly lessen the aqueous solubility of the polymers, especially if they are chemically linked to the polysaccharides. Since this material is alkali soluble, it would not hinder later hemicellulose extraction in any subsequent sulfate digestion. Further studies would be required to explore this hypothesis.

The so-called 'conditioning' of the hemicelluloses during the hydrolysis stage of the prehydrolysis sulfate process (18) may be explained, in part, in terms of a decrease in polymolecularity. The average chain length of the polyoses remaining in the fibrous woody material after two hours of hydrolysis is less than one third its initial value. This enhances both solubility and diffusion in the alkaline liquors of a sulfate cook. The shorter chain length may further aid in extraction of the polysaccharides

by providing a less viscous solution when dissolved by the pulping liquor within the secondary fiber wall, hence permitting freer effusion from the fiber. Finally, the lower degree of polymerization would probably lessen the tendency for redeposition of dissolved polysaccharide on the surface of the fibrous tissue (59).

The hydrolytic attack on the yield of cellulose is slight. A loss of about 1.5%, based on the wood, is incurred during 2 hours at 160°C. This loss is accounted for in reductions of the xylan and mannan contents of the alkali-resistant cellulose. The xylan associated with the cellulose preparations is reduced in amount by about 50%, and the mannan by 30% during this reaction.

Interestingly enough, of the total xylan content of black gumwood at any stage of hydrolysis, only a very small proportion is retained by the alkali-resistant cellulose. On the other hand, over 90% of the total mannan content of the wood remaining after any particular stage of the hydrolysis is found in the respective alkali-resistant cellulose. Hence, the mannan appears to be a cellulosic constituent which stoutly resists hydrolysis (61-63).

Although the loss of polyglucosan by the cellulose is negligible during the hydrolysis of the wood, a significant reduction in polymolecularity does occur. During 2 hours of reaction, the average cellulose chain length is reduced by 38%. About 80% of this decrease occurred in the first hour.

The shape of the hydrolysis curve, Figure 12, is typical of the heterogeneous hydrolysis of cellulose (60), and is generally explained on the basis of the classical structural theory. The rapid degradation in the early stages of reaction occurs in the amorphous regions of the polymer network. This is then followed by a much slower chain-length reduction in the crystalline areas. Due to the mercerizing treatments involved in the isolation of the celluloses, the true differences in crystallinity as measured by x-ray diffraction were partially masked.

In conclusion, it has been observed that both the cellulosic and hemicellulosic polysaccharides are hydrolyzed by the action of water at 160°C. on the wood. The hemicelluloses are very rapidly degraded and partially removed from the wood as soluble hydrolytic fragments, which are further reduced to simple carbohydrates in the medium. The cellulose is reduced in polymolecularity, but to a significantly lesser degree than are the hemicelluloses. Whereas the hydrolysis products of the hemicelluloses are dissolved from the wood, the loss of polyglucosan from the cellulose is insignificant during a 2-hour hydrolysis. However, it is apparent from the literature that prolonged or intense hydrolysis of the wood results in loss of cellulose on subsequent pulping and purification.

SUMMARY AND CONCLUSIONS

Through careful design of equipment and control of experimental conditions, the hydrolysis of black gumwood was effected at the constant temperature of $160 \pm 1^\circ\text{C}$. The hydrolysis was carried out for various time intervals ranging from 'zero' time up to 120 minutes. After each time interval the residual wood yield was determined, and the constituent polysaccharides isolated.

The isolation of the hemicellulosic polysaccharides followed a series of critically controlled chlorinations and alternate ethanamine extractions of the woody residues. Two fractions (5 and 16% hemicelluloses) were obtained from each hydrolysis stage according to their alkaline accessibility, and were extensively purified by alcoholic reprecipitation from solution. The alkali-resistant celluloses were isolated after a final delignification and extraction of the resulting residues.

In addition to determining the yields of the various fractions after each hydrolysis interval, the polysaccharides were subjected to quantitative chemical analysis and average chain-length determinations in order to follow the course of the hydrolytic attack.

The carbohydrates in the hydrolysis liquors were also investigated to determine their identity. Polysaccharide components from some of the liquors were further hydrolyzed, and the resulting hydrolyzates chromatographed to identify their component sugars.

The results of these investigations and the conclusions derived

therefrom on the course of polysaccharide hydrolysis during the aqueous treatment of black gumwood at 160°C. are summarized as follows:

The wood yield dropped nearly 30% during hydrolysis for 120 minutes, and was found to be a linear function of the logarithm of hydrolysis time. About 55% of the wood loss was due to the removal of hemicellulosic polysaccharides. The cellulose yield, based on the original wood, remained virtually unchanged.

The hemicelluloses removed during the 120-minute period represented about 70% of their original content in the wood. The rate of removal was constant over the first hour, being 3% of the weight of wood per 15 minutes of hydrolysis, but this rate dropped sharply during the second hour.

Simultaneous polymeric degradation of both the cellulose and hemicelluloses began as soon as the wood contacted water at 160°C. The average chain length of the hemicelluloses was reduced by about 33% in the first 15 minutes of reaction, and by 65% within the first hour. The decrease in the average D.P. of the cellulose was considerably less: i.e. 38% in 2 hours; eighty percent of this loss occurred within the first hour.

The hemicelluloses of black gumwood were found to be composed chiefly of xylan and uronic anhydride, with minor amounts of glucan, galactan, mannan, araban and possible rhamnan. Somewhat greater proportions of mannan were found in the 16% than in the 5% hemicellulose fractions. As the hydrolysis progressed a considerable increase in the amount of an acid-insoluble, noncarbohydrate was noted. This could be isolated from the woody

tissue remaining after the hydrolytic periods, and was removed together with the hemicelluloses. However, the only significant change in the relative carbohydrate compositions of these hemicelluloses even after the longest hydrolysis treatment was a drop of 50% in the uronic anhydride content of the 16% hemicellulose fraction.

The over-all rate of removal of the hemicelluloses from the wood follows no simple kinetic pattern. It appears to be related closely to the rate of depolymerization as the reaction progresses. The first order constant for the removal rate shows a marked increase over its initial value, reaches a maximum within 45-60 minutes, and then decreases sharply. The early rise is concomitant with the increased solubility and number of depolymerized polysaccharide chains available in the tissue. The later fall in the rate of solution appears to be a complex function, which depends upon fiber morphology and hemicellulose distribution, described by Lange and Asunmaa (58) and the probable retarding influences of closely associated noncarbohydrate materials indicated in this work, and presumably generated during the reaction.

In the hydrolysis, the hemicelluloses are at first solubilized as polymeric fragments which are precipitable from the hydrolysis liquor by alcohol. These fragments are then further reduced in size and ultimately form simple sugars and aldobiuronic acids, which may be separated chromatographically from the liquors. The hydrolysis also appears to convert the carbohydrates to acid-insoluble materials in the hemicellulose fractions that no longer show the usual carbohydrate properties. Condensation with reactive liquor components may play a role in their formation.

During the course of the hydrolysis, the yield of alkali-resistant cellulose is decreased by only 1.5% (based on the original wood). This loss may be attributed to a reduction in the amounts of retained xylan and mannan, which furnished the only sugar units other than glucose detectable in significant amount in the cellulose hydrolyzates. The occurrence of practically all of the mannan, remaining in the partially hydrolyzed wood, in the alkali-resistant cellulose fractions of the polysaccharides, is further evidence that it may be present in the cellulose chains, or at least closely associated with wood cellulose.

Although the cellulose yield of black gumwood is not appreciably decreased during hydrolysis, the significant reduction in chain length would probably be sufficient to cause a reduction in yield on subsequent sulfate digestion. The preconditioning of the remaining hemicelluloses for eventual extraction during pulping and alkaline purification is, in part at least, manifested in the striking decrease of the average degree of polymerization which occurs within 2 hours.

In conclusion, it appears that the major changes in the wood content and the D.P.'s of the hemicelluloses of black gum occur early in the hydrolysis treatment, and for the most part, within the first hour at 160°C. Inasmuch as this study was restricted to reactions occurring at a single temperature and was not integrated with subsequent pulping and purification sequences, any conclusions on optimum hydrolysis conditions would be premature. However, continued studies in this area should enhance the application of fundamental knowledge to future technological developments.

It is further noteworthy that although the hydrolysis of wood with water at 160°C. is effective in reducing both the content and polymolecularity of xylan-rich hemicelluloses, it is far less efficient in the removal of mannan. Hence, it is difficult to conceive of using such a process in the preparation of cellulose from coniferous woods. However, inasmuch as hardwood and softwood mannans may be considerably different in chemical behavior, this problem merits further investigation.

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APPENDIX

QUANTITATIVE CHROMATOGRAPHIC SUGAR ANALYSES

The cellulose and hemicellulose hydrolyzates were analyzed chromatographically according to the procedure of Piper and Bernardin (45). Due to inherent differences in the kinds and relative proportions of the sugars present in the hydrolyzates of these two classes of polysaccharides, the chromatographic procedures in the two cases were slightly different.

The hemicellulose hydrolyzates were developed on 9 by 24-inch strips of Whatman No. 1 filter paper in butanol-pyridine-water (10:3:3) for 60 hours, then air dried and developed further with ethyl acetate-acetic acid-water (9:2:2) for about 20 hours.

The cellulose hydrolyzates were developed on 7 by 24-inch strips of the same paper in a single 36-hour period, using ethyl acetate-acetic acid-formic acid-water (18:3:1:4).

A standard reference solution containing all the sugars to be analyzed at known concentrations, was applied on the same sheet together with the hydrolyzates to be analyzed. The volumes of reference solution were so chosen that each sugar component to be analyzed was present in varying amounts over the range of 10 to 200 γ . The hydrolyzates were spotted in such volumes that the amount of each sugar fell within this range. The reference sugars were applied alternately with the hydrolyzates across the sheet.

The fully developed chromatogram was sprayed lightly and uniformly with the spray reagent¹ using approximately 20 ml. per sheet. The sheets were air dried for about 10 minutes and heated at about 105°C. for 5 minutes or less. The spots were outlined in pencil under U.V. light² and cut from the sheet together with equal areas of paper blank found to be sugar-free under U.V. light. Each spot was eluted with 6 ml. (pipet or buret) of the reagent in 150-mm. test tubes by shaking vigorously for 15 to 20 minutes. The eluates were filtered through glass wool to remove suspended fibers, and color development was completed by heating in a boiling water bath--at least 30 minutes for pentoses and 45 minutes for hexoses. This final heating was carried out in test tubes (150 mm.) sealed with rubber stoppers covered with aluminum foil. The colored solutions were then cooled to room temperature, and their absorbances measured against the blank at 380 mm. A. B. & L. Spectronic 20 spectrophotometer was used for the measurements.

Absorbance values were plotted against the amounts of sugars used as the standards, and the unknowns were determined from the resulting linear graphs.

¹ Spray reagent and eluent: 0.4 g. o-aminobiphenyl (m.p. 47-49°C.) dissolved in 100 ml. reagent-grade glacial acetic acid, and 20 ml. distilled water.

² Mineralight, short wave U.V. Model S L 2537 with short wave, U.V. filter for pentoses; Burton hand light, with 4-watt, G.E. black-light lamps for hexoses.